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The influence of environmental characteristics on chemical concentrations

Ruimtelijke variatie in multimedia massabalansmodellen
De invloed van milieukarakteristieken op concentraties van stoffen in het milieu

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Contents

1 General introduction

Chemicals in the environment

Chemical substances are emitted, for example with the production of goods, with transportation, as pesticide or as waste product. The substances can be harmful for the human health or for the functioning of ecosystems: ecosystems can be disordered and certain species can extinct. To humans they can cause disorders, such as allergies, asthma, certain types of cancer, and reproductive problems. Whether a certain chemical substance causes harmful effects to the human health or to the functioning of ecosystems, depends on the toxicity of the chemical on the one hand, and on the dose at which humans or other organisms are exposed to the chemical on the other hand (Figure 1; Bro-Rasmussen, 1988; Van Leeuwen and Vermeire, 2007). Exposure of organisms to chemicals mainly occurs by breathing (air), eating (vegetables, meat), drinking water and skin contact.

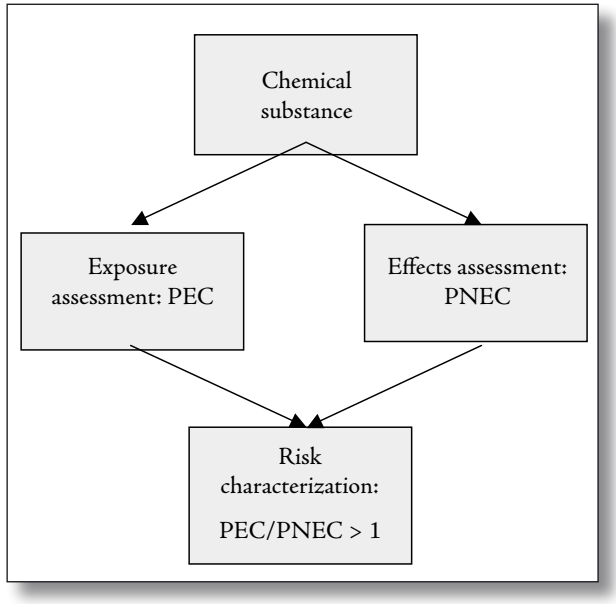


Figure 1: Risk characterization scheme for chemical substances. Whether a certain chemical can cause harmful effects to organisms, depends on its toxicity on the one hand (i.e. PNEC: predicted no-effect concentration), and on the dose at which organisms are exposed to the chemical on the other hand (i.e. PEC: predicted environmental concentration). If the ratio between PEC and PNEC exceeds a value of 1, a substance may form a risk.

Numerous chemical substances are on the market, with different emission patterns and different physical-chemical properties. Due to these differences, the substances do not behave similarly in the environment after being emitted (Mackay, 2001). They have the ability to be transported within and between the different environmental compartments (i.e. air, water, soil, sediment, biota), they can accumulate in a certain compartment, and they can be degraded by various abiotic and biotic processes. To assess the exposure levels of organisms to the chemicals, environmental concentrations of chemicals are required (Trapp and Matthies, 1998). For many chemical substances, concentration measurements in the different environmental compartments are scarce, or even entirely lacking. Besides, measurement data are always bound to a certain location in time and space. And due to the complex nature of degradation and transport processes of chemicals in the environmental system, it is not practicable to predict the concentrations of all chemicals at all times and all places. Therefore, fate of chemicals in the environment remains uncertain.

Multimedia mass balance models

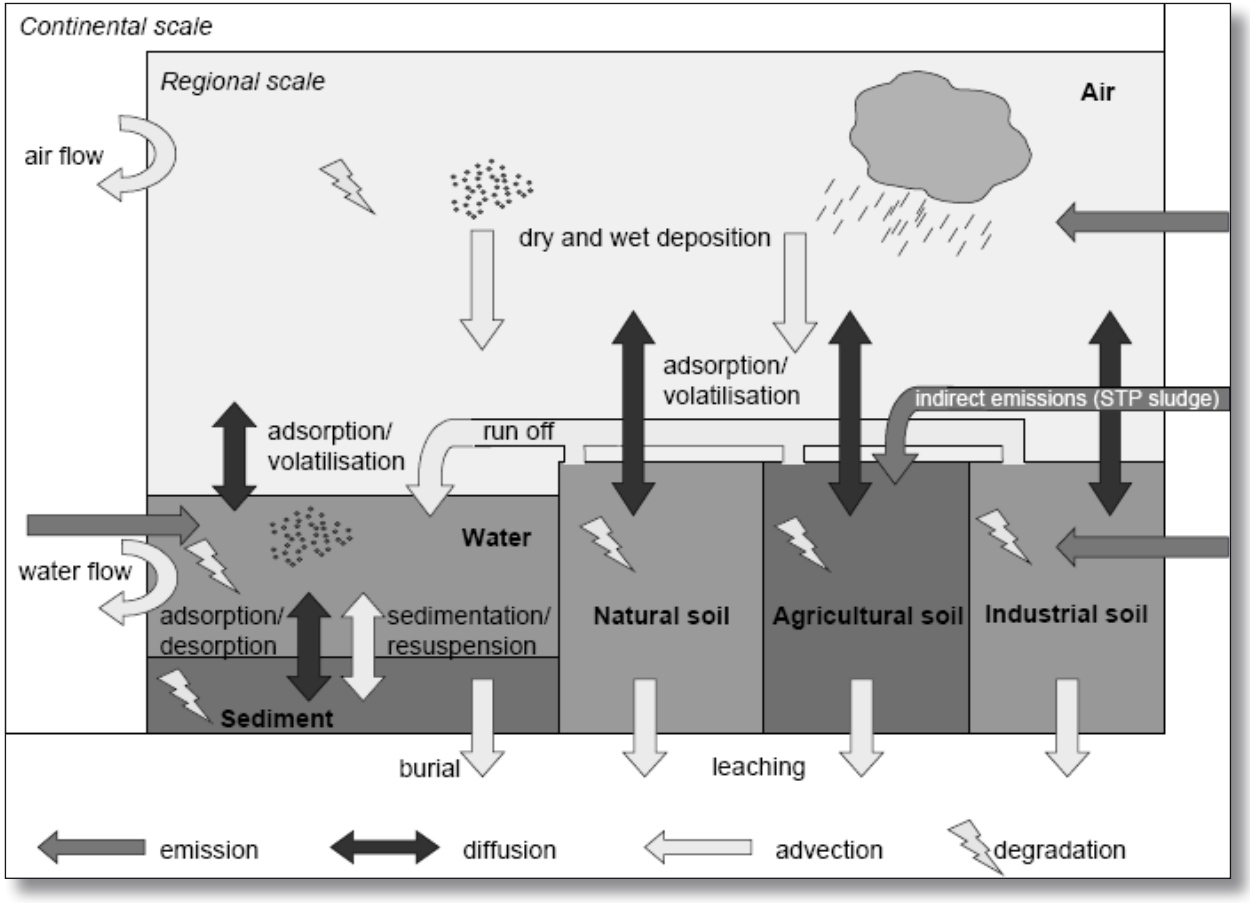
Instead of measurements, computer models are often used to estimate or predict the environmental chemical fate. Many different types of models are used for this purpose, of which the focus in this thesis is on multimedia mass balance models. This type of models predicts the environmental fate of chemicals on a relatively course scale. Other common terms for these models are 'box models', 'multimedia fate models' or 'Mackay models', after the originator of this modeling branch (OECD, 2004). Principally, in these models, the environment is represented as a set of homogeneous boxes or compartments, each representing a specific environmental medium (e.g. air, water, soil, biota). Substance exchange between the different compartments occurs by diffusive (i.e. spontaneous net movement of particles from an area of high concentration to an area of low concentration) and advective transport (i.e. with the flow of air, water or suspended particles). Within the compartments, the substance is being degraded by abiotic and/or microbial breakdown. The concentration of a chemical in a certain compartment can be calculated by formulating and solving a set of mass balance equations that describe the processes of emissions, degradation and inter-compartment transfer (Mackay, 2001). Physical-chemical substance property data (i.e. vapor pressure, solubility, octanol-water partitioning coefficient, degradation rate constants), environmental characteristics (i.e. climatic factors, soil conditions, land use characteristics) and emission data (emission compartments and intensities) serve as input to multimedia mass balance models.

The first multimedia mass balance models were developed in the late 1970s and early 1980s (Mackay, 1979; Mackay and Paterson, 1981; Mackay et al., 1985). Over the past decades, the use of these models to predict the environmental fate of chemicals has strongly increased. Multimedia mass balance models were originally developed for the screening and evaluation of the environmental fate of toxic substances and therefore these early models produced rather rough estimations of environmental concentrations (Cowan et al., 1995; Mackay, 2001). These models have proven to be very useful tools in chemical risk management for regulatory purposes due to their relatively low complexity together with their multimedia character. In the European Union, the EUSES model (Figure 2; Vermeire et al., 1997; 2005) is currently being used as a risk policy instrument, whereas in the USA, CalTOX (McKone, 1993) and the total risk integrated methodology (TRIM.Fate; US-EPA, 2002) are typically applied for this purpose. In this context, multimedia mass balance models are also used for "benchmarking" new and existing chemicals. Benchmarking is a relative approach for ranking chemicals by comparing model estimates (OECD, 2004). Environmental fate descriptors that are often used for the ranking of chemicals are the overall persistence (P_{ov}) and long-range transport potential (LRTP) of chemicals (Scheringer, 1996; Wania and Dugani, 2003; Fenner et al., 2005, Klasmeier et al., 2006). Beside their use in policy and legislation, multimedia mass balance models are of value for scientific goals. They can help understanding the behavior of substances in the environment, as well as in identifying data gaps (e.g. accurate physical-chemical properties or

model processes) concerning chemical fate (Newham et al., 2003).

The available multimedia mass balance models can be classified following different criteria. A classification method often used is based on the level of process complexity, for which four levels (level I to level IV) are suggested by Mackay and Paterson (1981; Van Leeuwen and Vermeire, 2007). In a level I model, a closed system is modeled, in which equilibrium partitioning as well as steady-state conditions are assumed. With increasing complexity, these assumptions are subsequently abandoned, finally resulting in level IV models, which represent dynamic, open environmental systems.

Figure 2: Schematic set-up the regional distribution model of EUSES (EC, 2004).



Another way of classifying multimedia mass balance models is by their spatial complexity. In the classical multimedia mass balance models, the environmental media are represented as single well-mixed boxes, within which the environmental conditions, emission intensities and concentrations are assumed to be the same in all places, laterally as well as vertically. However, in reality, environmental conditions as well as emission intensities do vary in space, resulting in chemical concentrations that differ from place to place. Due to the rapid development of geographical information systems (GIS), and the improved technical and computational opportunities, spatially resolved multimedia fate models have been developed since the 1990s. In 1995, Wania and Mackay tentatively screened the possibilities for introducing GIS in multimedia fate models (Wania and Mackay, 1995). More advanced models followed (Wania, 1996; Woodfine et al., 2001), and presently many different multimedia mass balance models exist, showing a wide variety in the extent to which environmental characteristics are described in spatial detail. Examples of well-known spatially explicit multimedia models are IMPACT-2002 (Pennington et al., 2005), BETR-Europe (Prevedouros et al., 2004), BETR-Global (MacLeod et al., 2005), MSCE-POP (Gusev et al., 2005), MCTM (Lammel et al., 2001) and G-CIEMS (Suzuki et al., 2005). A special type a spatial model is performed by ClimoChem (Scheringer et al., 2000) and ChemRange (Held, 2001; Scheringer et al., 2001), which distinguishes different lateral zones while neglecting longitudunal differences. Another specific sub-group is the group of spatially explicit fate models using river basins as the basic unit (Coulibaly, 2004; Suzuki et al., 2005), of which some focus on instream water quality (i.e. Great-er; Boeije et al., 1997; Feijtel et al., 1997). The models mentioned above do take spatial environmental variation into account, but at the same time, their complexity increases as well as their demand for input data. It is therefore not necessarily more useful or advisable to work with spatially resolved models. To enable a well-considered decision on the degree of the spatial environmental variation that has to be incorporated in a specific modeling study, one should have an idea of the effects of integrating this spatial variation on the model outcomes.

Several authors have explored the effects of incorporating spatial variation in multimedia mass balance models on the predicted environmental concentrations. For example, Wania and Mackay (1995) explored that in global fate modeling, the location and medium of emission, as well as several environmental parameters strongly influence the calculated global fate of substances. On a regional scale, the quality of results obtained from a regional environmental fate model for Canada was improved by the use of region-specific landscape parameters (Webster et al., 2004). Sensitivity analyses have been performed on landscape characteristics in multimedia mass balance models (Hertwich et al., 1999; Maddalena et al., 2001, Huijbregts et al., 2000). From the study of Hertwich et al. (1999) it appeared that model outcomes are more sensitive to the values of physical-chemical properties than to those of landscape characteristics. Huijbregts et al. (2000) also found that the major variation in predicted toxicity of atrazine, 2,3,7,8-TCDD and lead originates from a limited set of physical-chemical input parameters. Other authors explored the influence of the varia-

tion in single landscape characteristics on the spatial variation in model results. Sweetman et al. (2005), for example, examined the role of soil organic carbon in the global cycling of POPs, and Wania and McLachlan (2001) estimated the influence of forest characteristics on the overall fate of semi-volatile organic chemicals. The effects of spatial modeling on concentration predictions were often explored by comparing spatially explicit models with their non-spatial counterparts (Klepper and Den Hollander, 1998; Pennington et al., 2005). For example, Pennington et al. (2005) compared spatial versus non-spatial model outcomes for chemical emissions in Western Europe, and concluded that the non-spatial models are likely to be appropriate in general for assessing dispersed sources of emissions, except when large stagnant water-bodies are present in the model area. For assessing an emission source in a specific location, using models that are not spatially resolved can result in a biased estimation of exposure levels. Several authors (Hansen et al., 2006; Lammel et al., 2007; Hauck et al., 2008; Armitage et al.,2007) compared the outcomes of different spatial and non-spatial multimedia fate models. Armitage et al. (2007), for example, found good agreement between the spatial and non-spatial models for four PAHs and HCB in the European air compartments, while large discrepancies are found in the soil, water and sediment compartments. Cahill and Mackay (2003) summarized the use purposes of different model complexities. According to that study, the simplest models should be used for establishing partitioning tendencies and for rankings of chemicals, while more complex regional models provide adequate results if emissions occur to air or water. A high resolution model is preferred for local scale, dynamic simulations or if emissions occur to soil (Cahill and Mackay, 2003). However, from this study no clear indications are obtained of the effects of incorporating spatial input data on the model predictions.

Beside lateral variation in environmental conditions, emissions and concentrations of chemicals, also vertical spatial gradients can be distinguished within most environmental compartments (i.e air, Hertwich and McKone, 2001; soil, Cowan et al., 1995). However, the use of a single mass balance equation per environmental compartment implies that concentration differences within one compartment are neglected. Particularly for the soil compartment, this assumption often does not correspond with actual field situations. As a consequence of neglecting vertical concentration differences in soil, substance flows that relate to specific depths, such a volatilization and leaching, are under- or overestimated in standard multimedia mass balance models.

Aim of this thesis

Multimedia mass balance models can be useful for scientists and decision makers, because they provide an appropriate framework to evaluate the complex interactions between chemicals and the environment. The greatest challenge for multimedia fate models is to provide useful information without creating overwhelming demands for input data and producing outputs that can hardly be evaluated (OECD, 2004). In this context, the Parsimonius' principle: 'as simple

as possible, but as complex as necessary', can perfectly be applied in multimedia models. In literature, three criteria are often mentioned for determining the optimal spatial detail in multimedia mass balance models: 1) the availability of spatially explicit input data, 2) the preferred technical or computational model complexity and 3) the purpose of the modeling study (OECD, 2004). When determining the purpose of the modeling study, the preferred precision of the models outcomes needs to be chosen. And to achieve that precision, the preferred spatial detail in model outcomes has to be defined. Which spatial model detail is required to reach the desired detail in model outcomes, is partly dependent on the (expected) spatial variation in environmental concentrations in reality. This means that if a substance will be homogeneously distributed throughout a large area, a lower spatial detail is required to achieve the chosen precision in model outcomes than if the concentration of a substance will vary significantly among different locations within an area.

The spatial variation in environmental concentrations forms the general framework of this thesis. The magnitude of the spatial variation in environmental concentrations is dependent on various factors, like the spatial emission pattern, the emission compartment(s), and the substance(s) under consideration. A factor that may also play a determining role is the spatial variability in environmental conditions. The main goal of this thesis is to analyze the relative importance of the spatial variability in environmental conditions on the spatial variation in environmental concentrations. To this end, the aim is to indicate which factors influence the spatial variation in environmental concentrations, to which extent they are of importance, and how they ar related to the factor 'spatial variability in environmental conditions'. Based on the insights obtained from this information, the (expected) spatial variation in environmental concentrations can be predicted more reliably, and thus, it will be easier to decide which spatial model resolution is desirable for a certain study, given the purpose of the study.

Outline of the this thesis

Chapters 2 en 3 describe and validate a method for incorporating depth-dependent soil concentrations in multimedia box models. In Chapter 2, the implementation of exponentially declining soil concentrations with depth is described, and the effects of this model change on the predicted environmental concentrations is explored. In Chapter 3, the predicted exponential soil concentration profiles are compared with measured soil concentrations to validate the method.

Chapter 4 gives a description of the BasinBox model, a generic box model in which the study area is represented as a river basin that is subdivided into an upstream, midstream and downstream area. Calculations on 3175 hypothetical compounds in the Rhine river basin were performed to show the concentration differences between the upstream and downstream area of the river basin. The results of this study provide information on the relative influence of spatially variable emission intensities and environmental characteristics on the spatial concentration variation of chemicals, taking

into account different emission compartments, receiving compartments, and chemical substances.

Chapters 5 and 6 of this thesis describe two model intercomparison studies between spatial and non-spatial environmental models. These comparisons provide insight in the similarities and discrepancies between these two types of models. In the first study, a comparison is made between the non-spatial multimedia mass balance model SimpleBox, the spatially explicit model LOTOS-EUROS and measurement data for the POP-chemical PCB-153. The second study is an inter-comparison study between the P_{ov} and LRTP estimates of seven different environmental models. Based on these inter-comparison studies, the influence of grid cell size, emission variation and physical-chemical characteristics on the spatial variation in predicted concentrations, P_{ov} and LRTP ranking are evaluated.

In Chapter 7, the relative influence of substance properties and of environmental characteristics on the variation in concentrations of chemicals in Europe is compared. This was done for a combination of 200 randomly selected organic chemicals and 137 realistic European regions, representing a 250x250 km spatial scale. Stepwise multiple regression analysis was performed to determine the contribution of each of the individual input parameters on the total concentration variation. This chapter provides a clear overview of the relative influence of grid cell size, environmental compartment, physical-chemical properties, environmental characteristics, and emission compartment on the predicted variation in environmental concentrations caused by local emissions.

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2 Implementation of depth-dependent soil concentrations in multimedia mass balance models

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Abstract

In standard multimedia mass balance models, the soil compartment is modeled as a box with uniform concentrations, which often does not correspond with actual field situations. Therefore, the theoretically expected decrease of soil concentrations with depth was implemented in the multimedia model SimpleBox 3.0. The effects of this implementation on the model outcomes were explored for nine compounds in four environmental compartments. For compounds with a low penetration depth, the new model predicts substantially higher or lower concentrations in the vegetation compartment than the old model. For those compounds, predicted concentrations in surface water and air were higher in the new model, but the deviations from the old model were smaller than in the vegetation compartment. For compounds with a large penetration depth, the model adaptations show little effect.

No field study was carried out to validate the results of the model calculations, but we did collect measurement data on concentrations in vertical soil profiles from literature. According to those data, we concluded that the implementation of depth dependent soil concentrations might be a useful extension for steady state multimedia mass balance models. More field study has to be carried out to validate the model outcomes.

Introduction

As chemicals can pose serious risks to human health and the environment, it is important to predict their concentrations in all environmental media. An instrument often used for predicting the fate of chemicals in the environment is the multimedia fate model (Cowan et al., 1995; Wania and Mackay, 1999; Mackay, 2001). In this type of model the study area is represented by a number of homogeneous compartments, each representing a specific part of the environment (i.e. atmosphere, water, soil, sediment, biota). The concentration of a chemical in a certain compartment can be calculated by solving a set of mass balance equations that describe processes like emission, degradation and inter-compartment transfer.

The use of a single mass balance equation per environmental compartment implies that concentration differences within one compartment are neglected. Particularly for the soil compartment, however, this assumption often does not correspond with actual field situations. As a consequence of neglecting depth-dependent concentration differences in soil, substance flows that relate to specific depths, such as volatilization and leaching, are under- or overestimated in standard multimedia mass balance models. This problem was noted by Cowan et al. (1995), who suggested that it could be overcome by taking the chemical-dependent soil penetration depth as a working depth for the soil compartment. Brandes et al. (1996) have implemented this soil penetration depth in the multimedia fate model SimpleBox 2.0. This model implementation may yield more realistic values for concentrations in the topsoil and, hence, better estimations of volatilization mass flows. However, transport from soil to surface water and groundwater, and uptake by plants may still be under- or overestimated. Similarly to the soil penetration depth, Hertwich and McKone (2001) described the use of height-dependent air concentrations in multimedia fate models.

McKone and Bennett (2003) proposed a way to calculate chemical fluxes from the soil compartment, based on a layered soil model in which chemical concentrations decline exponentially with depth in each soil layer. Assuming steady-state conditions, a fixed concentration boundary condition and uniform soil properties to depth z, the vertical gradient of concentration c in a certain soil layer is described by the equation

$$c(z) = c_0 e^{-z/d_p}, \text{ with } \quad d_p = \frac{v_e + \sqrt{v_e^{\,2} + 4kD_e}}{2k}$$

Equation 1

with c_o being the chemical concentration at the top of the soil layer and d_p being the characteristic soil depth or soil penetration depth; v_e describes the effective advection velocity ($m.s^{-1}$), De the effective diffusive coefficient ($m^2.s^{-1}$), and k stands for the degradation rate constant of the compound in a soil (s^{-1}). These terms are controlled by the physical-chemical properties of the compound, and the characteristics of the soil.

We propose to use the theoretically expected exponential decrease in soil concentrations to correct the intermedia mass flows in multimedia mass balance models by introducing correction factors that account for the deviation of depth-dependent soil concentrations from the depth-averaged concentration. The objective of

this study is to explore how implementation of depth-dependent soil concentrations affects the outcome of the standard multimedia mass balance models. To this end, the theoretically expected decrease of soil concentrations with depth was implemented in the multimedia fate model SimpleBox 3.0 (Den Hollander et al., 2004). The effects of this change on the predicted environmental concentrations are explored with a number of test chemicals. Predicted environmental concentrations (PECs) calculated by the model with depth-dependent soil concentrations are compared to the PECs following from the 'classic' SimpleBox calculations with depth-averaged soil concentrations.

Methods

The concept of exponentially decreasing soil concentrations was implemented in SimpleBox 3.0 using correction factors for the transport coefficients for a number of processes. The predicted steady-state concentrations in the soil, air, water and vegetation compartment were chosen as the model outcome of interest. Values calculated by the new and the old model are compared to assess the effect of the modification.

Model description

SimpleBox is a nested level III and level IV 'Mackay type' multimedia mass balance model consisting of ten environmental compartments in regional, continental and global scales (Brandes et al., 1996; Den Hollander et al., 2004). It is a generic model in the sense that it can be customised to represent specific environmental situations, while the default settings of the regional and continental scales in the model are set to match the European Union procedures for the evaluation of substances. Based on differences in land use types, three kinds soil compartments are distinguished on each spatial scale, distinguishing natural soils, agricultural soils and other (urban) soils. SimpleBox has no vertical segmentation of the soil compartment, which implies that soil characteristics are assumed to be constant with depth. Instead, SimpleBox calculates soil penetration depth as in Equation 1 as a basis for setting a substance-specific depth of the soil compartment. Values for v_e and D_e are calculated as sums of advections and diffusions in the gas phase, water phase and solid phase of the soil, assuming thermodynamic equilibrium at all times. The procedure described by MacLachlan et al. (2002) was applied, using their parametrization. The modifications described in this paper use the thus calculated soil penetration depth as input. The modifications were implemented in all types of soil compartments on all scales, but the example calculations used here focus on the agricultural soils on the regional scale only.

Model adaptation

Assuming an exponential decrease of soil concentration with depth as in (1), the depth-averaged soil concentration <c> is obtained by integration of (1) and subsequent division by the total depth d_t:

$$< c >= \frac{1}{d_t} \int_0^{d_t} c(z)dz = c_0 \frac{d_p}{d_t}\left(1 - e^{-d_t / d_p}\right)$$

Equation 2

Equations 1 and 2 can be combined into the following expression for the concentration at a certain depth z:

$$c(z) = < c > \frac{d_t / d_p}{1 - e^{(-d_t / d_p)}} e^{(-z / d_p)}$$

Equation 3

For transport processes that take place at a specific depth level, rather than equally distributed over the soil depth, the transport coefficients were corrected by a factor c(z)/<c>:

$$TRANS'(z) = TRANS \frac{c(z)}{< c >} = TRANS \frac{d_t / d_p}{1 - e^{(-d_t / d_p)}} e^{(-z / d_p)}$$

Equation 4

with TRANS'(z) being the new transport coefficient for a process at depth level z and TRANS being the conventional transport coefficient for this process.

Depth levels of the transport processes from the soil compartment

In SimpleBox, four types of transport processes occurring from the soil compartment are distinguished: volatilization to air, leaching to groundwater, transpiration to vegetation, and run-off to surface water. This single run-off term, based on the average concentration in the soil compartment, accounts for all advective transport processes occurring from soil to surface water (Den Hollander et al., 2004). As mentioned above, the purpose of this paper is to take into account vertical differences in soil concentrations to describe the outgoing transport flows. Therefore, a distinction was made between erosion and surface runoff at the soil surface (z = 0) and drainage run-off at a specific drainage depth (z) in the new model. In the new model, we have defined 20% of the total water flow from soil to surface water as surface run-off, and the remaining 80% as tube drainage. This reflects the situation in Dutch agricultural soils (Tiktak et al., 2003). In some chemical fate models run-off is supposed to occur within a surface layer with an arbitrary thickness of 0.5 (Crawford and Donigian, 1974), 1.0 (Leonard and Wauchope, 1980) or 2.5 cm (Steenhuis and Walter, 1978). Using the equations depicted above, a correction factor for such a layer could be developed as well, but due to the lack of justification of these values, in the new SimpleBox model the concentration at the upper boundary of the soil compartment was used. The drainage depth level can be chosen by the model user, based on available information about the level at which drainage tubes are found. For the Netherlands this is around 1 m below the soil surface.

Volatilization and leaching take place at the upper and lower boundaries of the soil compartment, respectively. A depth level of 40 cm was chosen for the description of the transpiration flow to vegetation in agricultural soils, because this is the depth at which the highest plant root activity is expected in Dutch grasslands. Both the vertical root distribution of plants in different biomes (Jackson, 1996) and the maximum rooting depth (Candell et al., 1996) have been studied, but unfortunately, the relative activity of roots at

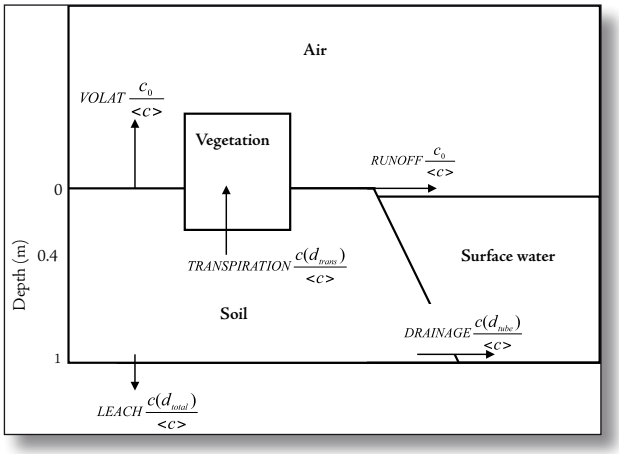

Figure 3: Schematic representation of the processes occurring from the soil compartment in the new SimpleBox model.

different depths is yet unknown. The structure of the root system and the water availability are expected to be important factors for this distribution. In general it may be expected that the deepest roots contribute most substantially to the total water uptake. Since grasslands cover a large part of the soil surface in the Netherlands (70%; Mulder et al., 2003), and grass roots extend about 40 cm deep (Jackson, 1996), this depth level was chosen for the transpiration flow in agricultural soils. For forested areas, the highest water uptake activity will be at a depth of about 80 cm, because trees generally have longer roots (Jackson, 1996). Therefore, for natural soils, 80 cm is suggested as the transpiration stream depth level.

Figure 3 shows a schematic representation of the transport processes occurring from the soil compartment in the new model and in Table 1 these processes are listed with their related depth levels and the corresponding correction factors.

Model calculations

To explore the effects of the model adaptations described above, the outcomes of the calculations performed with the old and the new SimpleBox model were compared. For all environmental parameters the default values of SimpleBox 3.0 were used in the calculations, except for two: first, the effective soil depth was set to 1 m for agricultural soils in the new model, while in the old model a depth of 0.2 m was used. This change was made to facilitate the implementation of

Table 1: Transport processes occurring from the soil compartment with their relevant depth levels and corresponding correction factors.

Transport process	*Relevant depth z*	*Corresponding correction factor*
Volatilization	*z=0 (air/soil interface)*	*(dt/dp)/(1-exp(-dt/dp))*
Leaching	*z=dt (lower boundary)*	*[(dt/dp)/(1-exp(-dt/dp))]exp(-dt/dp)*
Surface run-off / erosion	*z=0 (air/soil interface)*	*(dt/dp)/(1-exp(-dt/dp))*
Drainage	*z=1m (tube depth)*	*[(dt/dp)/(1-exp(-dt/dp))]exp(-dp)*
Transpiration	*z=0.4m (rooting depth)*	*[(dt/dp)/(1-exp(-dt/dp))]exp(-0.4dp)*

Compound	*Vapor pressure at 25 °C (Pa)*	K_{ow}	*Degradation rate constant in soil (s^{-1})*	*Penetration depth in standard agricultural soil (m)*[1]
Atrazin[2]	3.85×10^{-5}	4.04×10^{2}	1.64×10^{-7}	0.029
Bentazon	4.60×10^{-4}	2.19×10^{2}	5.01×10^{-7}	0.017
Fentin acetate	8.32×10^{-5}	4.50×10^{3}	3.09×10^{-7}	0.01
Fluazinam	7.35×10^{-6}	3.63×10^{3}	5.77×10^{-8}	0.028
Chloridazon	6.00×10^{-5}	1.38×10^{1}	1.25×10^{-7}	0.22
2,3,7,8-Tetrachloro-dibenzo-p-dioxin (TCDD)[3]	2.00×10^{-7}	6.31×10^{6}	1.14×10^{-8}	0.050
Di-(2-ethylhexyl)phtalate (DEHP)	1.10×10^{-10}	3.02×10^{7}	1.17×10^{-7}	0.016
1,2-Dichloroethane (EDC)	7.30×10^{-2}	2.88×10^{1}	8.89×10^{-8}	0.330
Linear alkyl benzene sulfonates (LAS)	1.00×10^{-6}	9.12×10^{1}	2.67×10^{-7}	0.04

[1] as calculated in Equation 2; [2] data source for pesticides: Rotard et al., 1994; CTB, 2004; [3] data source for industrial compounds: Berding, 2000

Table 2: Physical-chemical properties of the substances used in this study.

tube drainage at a depth of maximum 1 m in the model. Second, the water absorption rate for agricultural vegetation was set to 9.32×10^{-9} m/s, correcting a clearly erroneous default value suggested in SimpleBox. In this study only standard emissions to agricultural soils were assumed to take place, to enable comparison of the effects of the model adaptations on the fate of the different substances. The reason for using the same emission scenarios for all compounds is that the mode of entry has been shown to be a controlling factor in the extent to which environmental parameters affect multimedia fate model outcome (Webster et al., 2004; Mackay et al., 1996). The substances used in this study are listed in Table 2, together with their most relevant properties. These substances were chosen to cover a wide range in hydrophobicity and volatility.

Results

In Figure 4 the outcomes of the new SimpleBox model are compared to those of the old model. For four compartments (air, surface water, agricultural soil and agricultural vegetation), the ratio between the concentrations as predicted by the new and the old model is shown. Because different values for the effective soil depth were used in both models, the predicted soil concentrations corresponded to different soil volumes and consequently could not be compared straightforwardly. Therefore for the new model, the concentrations in the upper 20 cm were derived from integration of the predicted concentrations in the total soil com-

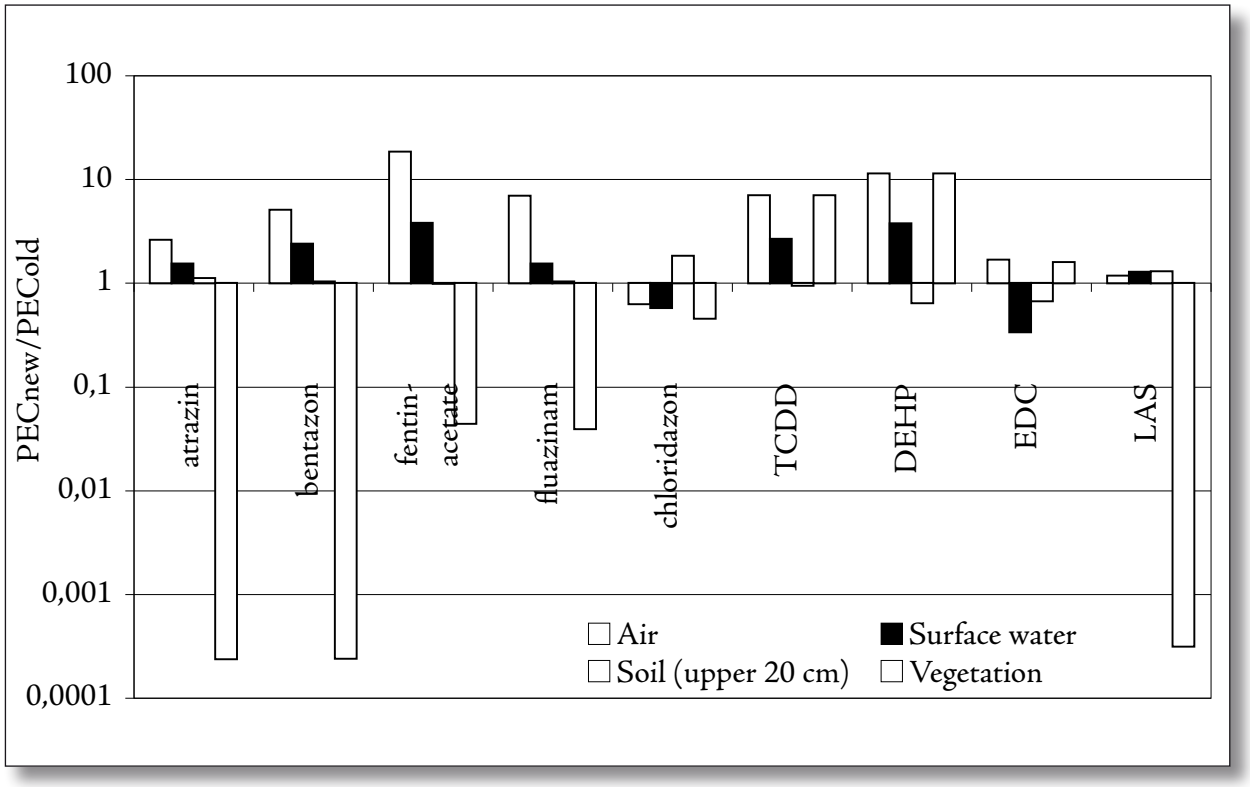

Figure 4: Ratios between predicted environmental concentrations of the new and the old model (PECnew/PECold) for four model compartments.

partments over the upper 20 cm. In Figure 4 this value is compared with the outcome of the old model.

The new model predicts substantially lower concentrations in the vegetation compartments for atrazin, bentazon, fentin acetate, fluazinam, chloridazon and LAS than the old model (ranging within one order of magnitude for chloridazon up to three orders of magnitude for atrazin and bentazon). On the contrary, the concentration ratio between the new and the old model is larger than one for TCDD, DEHP and EDC, with a factor of eight, ten and two, respectively. Concentrations in the soil compartment are not significantly affected by the model adaptations; only chloridazon and LAS show slightly higher predicted concentrations in the soil compartment, whereas DEHP and EDC concentrations in the soil are predicted somewhat lower (all within one order of magnitude). For the air compartment, the new model predicts higher

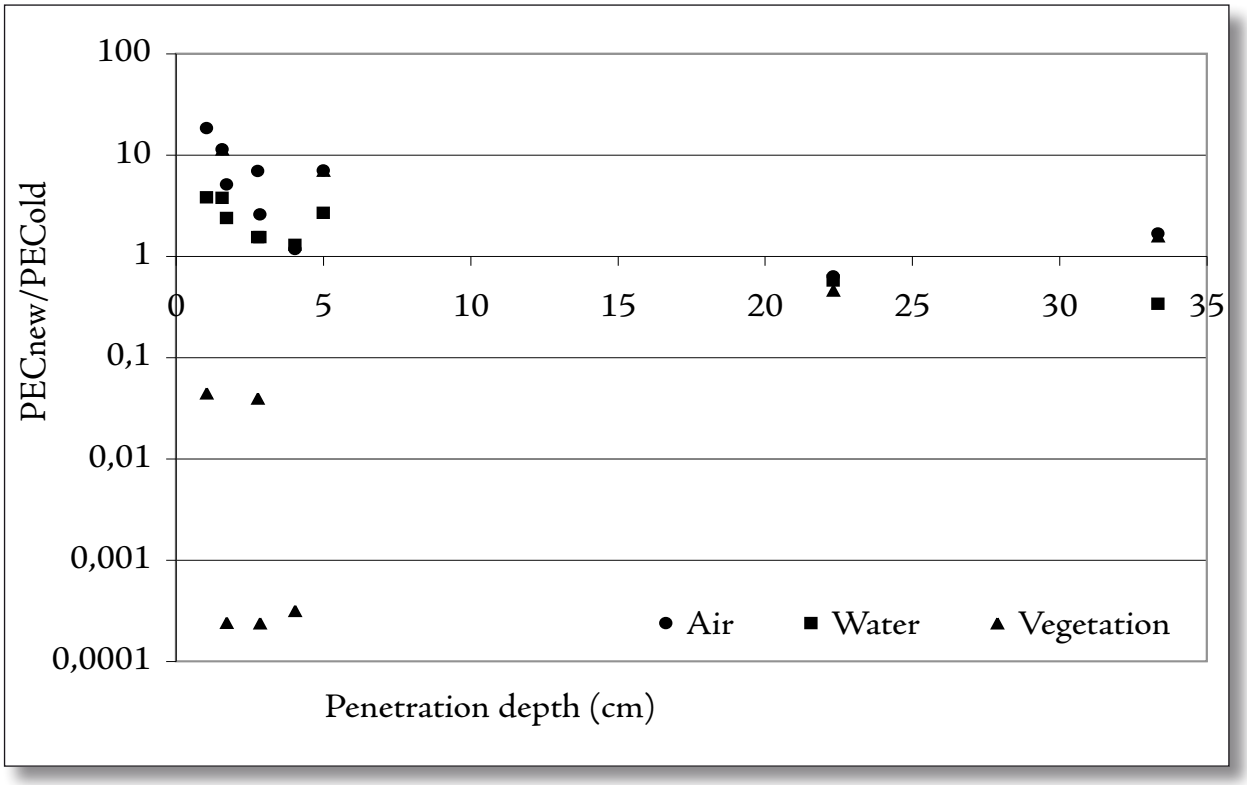

Figure 5: Relation between the effects of the model adaptations on the predicted environmental concentrations and the soil penetration depth in agricultural soils.

concentrations for atrazin, bentazon, fentin acetate, fluazinam, TCDD, DEHP, EDC and LAS and lower ,concentrations for chloridazon. The differences between the model outcomes for this compartment range in a maximum order of a magnitude of two.

Higher concentrations in the surface water compartment of the new model are predicted for atrazin, bentazon, fentin acetate, fluazinam, TCDD, DEHP and LAS and lower for chloridazon. The highest effects are found for bentazon, fentin acetate, TCDD and DEHP, but the deviations from the old model lay all within one order of magnitude. To explore possible correlations between the effects of the model adaptations and the soil penetration depths of the compounds, the ratios between air, water and vegetation concentrations predicted by the new and the old model are plotted against their penetration depth in Figure 5.

Figure 5 shows that for compounds with a high soil penetration depth (EDC and chloridazon), the ratio between the predicted concentrations only slightly differs from a value of one. Particularly for the vegetation compartment, the model outcomes of the new model show large deviations from those of the old model for compounds with a low soil penetration depth. In this compartment, both higher and lower predicted concentrations are present in the new model with regard to the old model. For the air and particularly for the water compartments this trend is less clear. The outcomes for the compounds with a low penetration depth are all higher in the new model than in the old model. However, for the surface water compartment, the differences between both models lay all within an order of a magnitude of one; for the air compartment the differences are predominately somewhat higher, up to an order of a magnitude of two. In general, predicted environmental concentrations of the compounds with a low soil penetration depth (atrazin, bentazon, fentin acetate, fluazinam, TCDD, DEHP and LAS) show larger differences between the old and the new model than the compounds with a high soil penetration depth (EDC and chloridazon).

Discussion

We introduced correction factors for the transport coefficients to account for the variation of soil concentrations with depth. In this way it was possible to predict intermedia transport flows based on the concentration at the related depth level rather than on the bulk soil concentration, without introducing extra compartments in the model. For scenarios with only soil emissions these modifications appear to have significant effects on the model outcomes.

Ratios between predicted environmental concentrations

For the four compartments studied, the ratio between the predicted environmental concentrations of the new and the old model will be discussed in this section.
The average soil concentrations predicted by the new model do not deviate significantly for any compound from those predicted by the old model. For the compounds with a low soil penetration depth, the influences of the different transport processes on the soil concentration balance each other: due to higher predicted concentrations in the top soil, the volatilization flow and the run-off flow are larger in the new model than in the old model. On the other hand, the groundwater leaching flow and, in most cases, also the transpiration flow is smaller in the new model. A combination of those four fluxes does not lead to significant concentration changes in the new model with regard to the old model. For compounds with a high soil penetration depth, the size of the different transport fluxes from soil is not strongly affected due to the model adaptations, resulting in more or less similar concentrations in the soil compartments of both models.
In most cases, also values larger than one for the PECnew/PECold ratio in the surface water compartments are predicted. Causes of this trend are first, the enlarged run-off flow from the soil compartment and, second, the increased atmospheric deposition flow due to higher atmospheric concentration levels. Exceptions are EDC and chloridazon. Due to their large soil

penetration depth, tube drainage is a more important transport route than surface run-off for these compounds. Because the concentration at the drainage depth level is lower than the bulk soil concentration, lower concentrations in surface water are predicted in the new model than in the old model.

In the air compartments, the new model predicts higher concentrations for all compounds but chloridazon. This is due to the higher soil volatilization flow, resulting from higher predicted concentrations at the soil-air interface. For the exceptional case of chloridazon, soil to water transport (drainage) and subsequent volatilization from surface water, rather than direct soil to air volatilization, appears to be the dominant route from soil to air, resulting in lower air concentrations. For five compounds, the new model predicts lower concentrations in agricultural vegetation. This is due to a lower transpiration stream flow, if based on the concentration at 40 cm below the soil surface. For the other three compounds, higher vegetation concentrations are predicted. In those cases, for TCDD, DEHP and EDC atmospheric deposition is a dominant transportation route to vegetation. In an earlier study of Trapp and Matthies (1995) it was already concluded that uptake from air was the major source for TCDD accumulation in vegetation, which agrees with the model outcomes of the current study.

Comparison of model outcomes to measurements

In this study, no validation of the model outcomes to field measurements was performed. We do believe that the removal mass flows from soil as computed in the new model are more realistic than the mass flows in the old model. However, isolated mass flow measurements which could be used to check if this is true were not available. Lacking direct measurement of mass flows, model improvement can only be deduced from improved prediction of concentrations in secondary compartments (air, water, vegetation). Field studies in which not only concentration measurements in soil were performed, but also in other environmental compartments, are scarce. The same applies to field situations for which long term emission scenarios are known, and for which the emissions have been constant in time. It is strongly recommended that a validation study will be done in future.

One way to get a feel for the degree of realism of the present model is to compare the theoretically expected exponential decrease of soil concentrations with depth with field observations. To this end we collected measurement data on concentrations in vertical soil profiles from literature. Several soil profiles with measured chemical concentrations at different depths were collected (Rotard et al., 1994; Cousins and Mackay, 1999; Vikelsøe et al., 2002). For each of those the best-fitting trend line describing the relationship between depth and concentration in the soil profile was calculated, which for most soils appeared to be an exponential fit. In Figure 6 an example is given of some measured concentration profiles of three different PCB's in the soil of the Danish agricultural and natural grasslands (Vikelsøe et al., 2002). From these measurement data, one can conclude that (i) soil concentrations do decrease with depth, and (ii) this decrease might be described with an exponential function. However, the empirically observed penetration

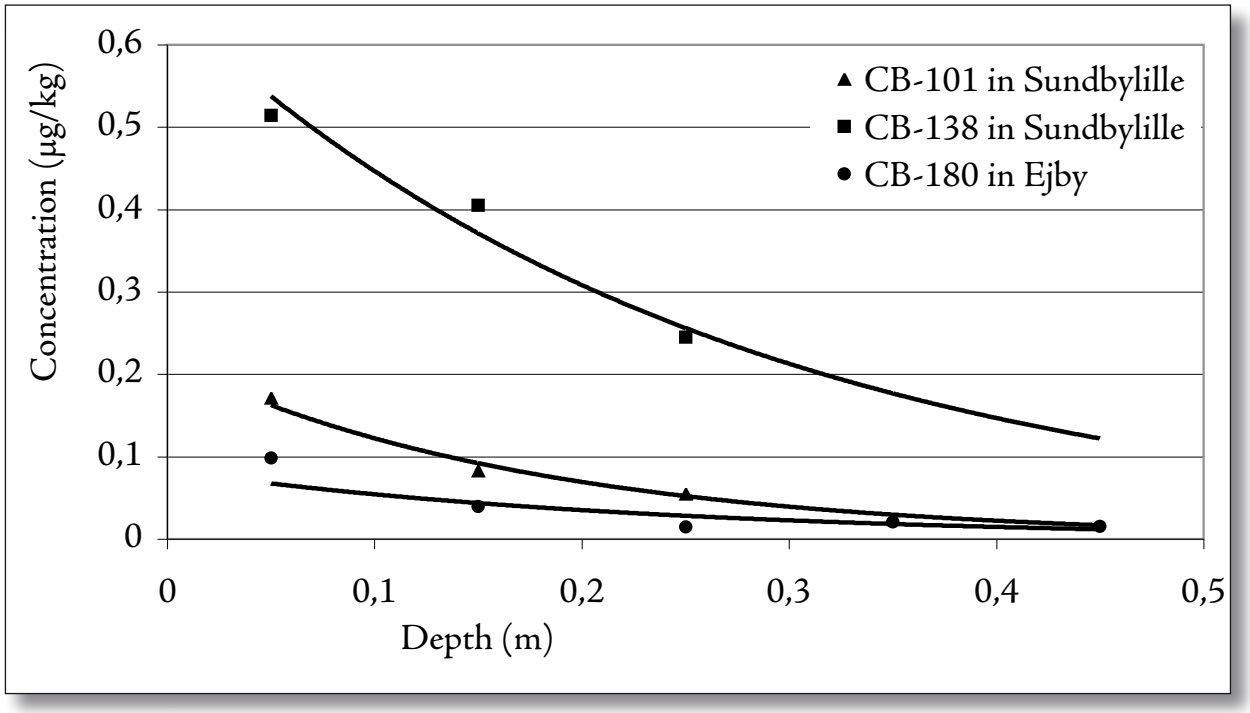

Figure 6: Measured concentration profiles of three different PCBs in the soil of the Danish agricultural grassland Sundbylille and the grassland nature reserve Ejby (Vikelsøe et al., 2002).

depths do not seem to agree well to the predicted penetration depth, as used in the model. The model tends to calculate smaller penetration depths than apparent from field observations.

Reasons for this may be that effective advection- and diffusion rates are underestimated and/or degradation rates are overestimated in the model. The calculation of the penetration depth in the model (Equation 1) uses solid-water and air-water partition coefficients, soil organic carbon fractions, soil porosities and soil water contents, and solid phase advectivities and diffusivities, all of which are hard to get for field conditions. Large discrepancies between calculated and measured penetration depths should, therefore, be anticipated. It must be noted that the theoretically expected exponential decrease of soil concentrations with depth is based on a number of doubtful assumptions. Exponential decrease in concentrations is expected only at steady state, which occurs seldom in reality, particularly for the very persistent PCBs, for which steady state takes long to establish. In addition, environmental conditions (e.g. meteorology) are usually not constant

in time, but vary. Moreover, soil parameters, particularly the effective advection velocity, effective diffusion coefficient and degradation rate constant are likely to change with depth, whereas the model assumes them to depth invariant. This will shatter the exponential shape of the decline. These factors could limit the reliability of the theoretically developed values for the soil penetration depth.

Nevertheless, we feel that the credibility of multimedia fate modeling could benefit from taking account of the knowledge that generally concentrations in soil are not constant, but tend to decrease strongly with depth. It is evident that more research is needed before penetration depths can be predicted adequately for this purpose. A number of input parameters that strongly influence the effect of the correction factors introduced need more attention. The emission scenario, the fraction organic carbon, the degradation constant, the depth levels of the drainage and the transpiration stream, and the relative importance of surface run-off and drainage are crucial for the model outcome. For site-specific risk assessment, detailed information can lead to a reliable value for the soil penetration depth and for the depth levels at which the main transport processes occur. However, more research is needed before values can be suggested that are suitable for generic risk assessment.

Correlation of effects of the model adaptation with soil penetration depth

Compounds that are readily degradable and relatively immobile do not have a high soil penetration depth. For those compounds, the concentration at the depth levels at which the exit flows occur deviate most from the bulk concentration. Consequently, for those compounds the model adaptations are expected to have the greatest effect on the model outcomes. However, more factors play a role. Even if only emissions to soils are assumed, the relative importance of certain transport processes in determining their environmental fate varies widely among different substances. For hydrophilic compounds, leaching, transpiration and run-off are important transport processes, while for volatile compounds, volatilization is most important. For well degradable compounds, degradation is an important 'removal route' while intermedia transport is less important to their fate. Summarizing, each factor that reduces the soil penetration depth of a compound also reduces the relative importance of the main transport processes that apply for that compound. Therefore, the relationship between the effects of the model adaptations and the substance properties cannot be predicted straightforwardly. In the example calculations, generally, the greatest effect of the model adaptations was observed for substances with the smallest penetration depth (Figure 5). Substances with a large penetration depth showed little effect. Nevertheless, more data are needed before any statistically valid extrapolations can be made.

It can be concluded that the implementation of depth dependent concentration differences in soils using the method proposed in this article, might be a useful extension for all standard multimedia mass balance models. The concept described in this paper, viz. that the consequences of vertical non-uniformity in soil concentrations for removal fluxes from soil can be

accounted for by adjusting mass transfer coefficients on the basis of estimated soil penetration depths, can easily be implemented in any steady-state multimedia fate model.

Acknowledgements
This work originates from a meeting of the SETAC task force on multimedia modeling in Leuven, 1994, where use of concepts of penetration depth and Damköhler depth in multimedia mass balance models was discussed. We acknowledge the input from the particpants of this meeting, especially Louis Thibodeaux, Don Mackay and Tom McKone.

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3 Validation of predicted exponential concentration profiles of chemicals in soils

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Abstract

Multimedia mass balance models assume well-mixed homogeneous compartments. Particularly for soils, this does not correspond to reality, which results in potentially large uncertainties in estimates of transport fluxes from soils. Corrections of transport fluxes from soils, based on a theoretically expected exponential decrease of chemical concentrations with depth, have been proposed, but hardly tested against empirical data. In this paper, we explored the correspondence between theoretically predicted soil concentration profiles and 84 field measured profiles. In general, chemical concentrations in soils appear to decline exponentially with depth. In half of the cases, values for the chemical specific soil penetration depth (d_p) were predicted within one order of magnitude. Over all, the reliability of multimedia models will improve when taking into account depth-dependent soil concentrations, the d_p-values estimated either based on local conditions or on a fixed d_p-value, which we recommend to be 10 cm for chemicals with a log K_{ow} > 3.

Introduction

After emission to the environment, chemicals may spread among all environmental compartments. As they can pose serious risks to human health and the environment, it is important to get insights in the behavior of those chemicals. Multimedia fate models are tools often used for predicting the fate of chemicals in the environment (Cowan et al., 1995; Mackay, 1991; Wania and Mackay, 1999). In this type of model the study area is represented by a number of homogeneous compartments, each representing a specific part of the environment (i.e. atmosphere, water, soil, sediment, biota). The concentration of a chemical in a certain compartment can be calculated by solving a set of mass balance equations that describe processes like emissions, degradations and inter-compartment transfer.

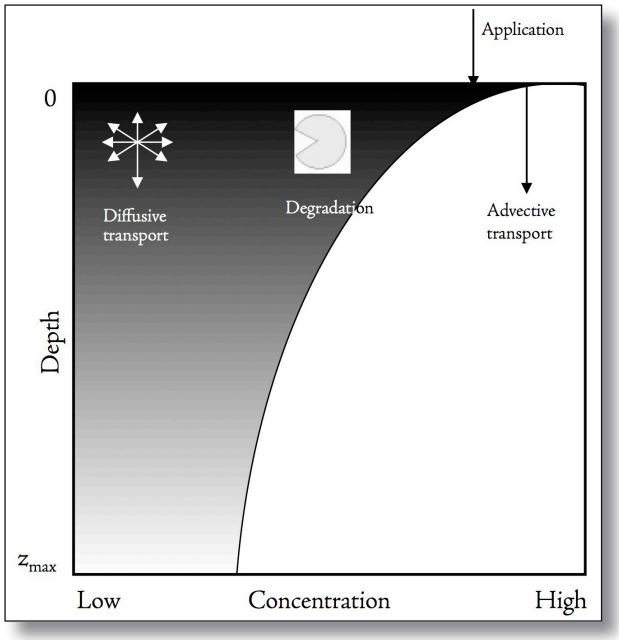

Figure 7: Schematic representation of an exponential soil concentration profile and the processes taking place in the soil.

The use of a single mass balance equation per environmental compartment implies that concentration differences within one compartment are neglected. Particularly for the soil compartment, this assumption often does not correspond with actual field situations. As a consequence of neglecting depth-dependent concentration differences in soils, substance flows that relate to specific depths, such as volatilization and leaching, are expected to be misestimated in standard multimedia mass balance models (Hollander et al., 2004).

Since the transport of chemicals towards the soil surface, either by direct emissions or by atmospheric deposition, is an important aspect of multimedia fate models, and since they are the most static of all environmental compartments, it is expected that chemical concentrations in soils usually decline with depth. This situation is displayed schematically in Figure 7. Some multimedia fate models adapt to this situation by introducing layered soils, e.g. the CalTOX model contains a 'ground surface soil layer', a 'root-zone soil layer' and a 'vadose zone soil layer' compartment (McKone, 1993). The advantages of a layered soil compartmentation are that different concentrations can be calculated for each layer, and that layer-specific soil conditions can be taken into account. However, within each layer still homogeneous conditions and concentrations are assumed. Besides, introducing more compartments in

the model will increase model complexity, which for simple screenings of chemical behavior and ranking purposes of relative chemical risks may be undesirable (Cahill and Mackay, 2003).

McKone and Bennett (2003) applied the steady-state solution of the general transport equation to describe the theoretically expected change of concentrations in soil with depth, based on the physical-chemical properties of the compound and on the environmental circumstances. Assuming steady-state conditions, a fixed concentration boundary condition and uniform soil properties to depth z, this vertical gradient of concentration c in a certain soil layer is described by the equation

$$c(z) = c_0 e^{-z/d_p}, \text{ with } \quad d_p = \frac{v_e + \sqrt{v_e^{\,2} + 4kD_e}}{2k}$$

Equation 5

with c_o being the chemical concentration at the top of the soil layer and d_p being the characteristic soil penetration depth; v_e describes the effective advection velocity ($m.s^{-1}$), D_e the effective diffusion coefficient ($m^2.s^{-1}$), and k stands for the degradation rate constant of the compound in a soil (s^{-1}). Hollander et al. (2004) implemented this equation in SimpleBox 3.0 in order to yield better estimates of mass flows occurring from the soil compartments to the air, water and groundwater compartments.

Implementation of this theory can also be useful for other multimedia fate models and even for totally different modeling purposes, like vadose zone pesticide transport modeling (e.g. Chu and Mariño, 2004) or local scale plant uptake models (Paterson and Mackay, 1994; Smith and Jones, 2000) to calculate substance flows correctly. However, in order to be a valuable modeling tool, the theoretically predicted soil concentration profiles should correspond with actual field situations. The objective of this study is to explore to which extent theoretically predicted steady-state soil concentration profiles correspond to soil concentration profiles measured in the field. To this end, literature data on depth dependent soil concentrations were collected. It was first investigated to what extent the measured soil concentration profiles show an exponential decline with depth. Secondly, we investigated to what extent the measured soil concentration profiles fit to the theoretical exponential functions under comparable environmental conditions. Steady-state situations are regarded, on which the theory originally applies, as well as non steady-state situations. By regarding steady-state as well as non steady-state situations, we tested the validity of the steady-state theory.

Methods

Measured soil concentration profiles

Literature data were collected on measured soil concentration profiles of several organic compounds. 84 Soil concentration profiles were collected from 17 locations and nine literature sources (Atanassova and Brümmer, 2004; Azevedo et al, 2000; Cousins et al.,

1999; Gocht et al., 2001; Landry et al., 2005; Rotard et al., 1994; Van Hees et al., 2005; Vikelsøe et al., 2002; Wilcke et al., 1996). The locations of the measurement sites and the compounds considered are given in Appendix A1. In that table, also the parameter values on environmental conditions required for predicting soil penetration depths according to Equation 5 are listed for the different sites, which are the rain rate, the environmental temperature, and the average organic carbon content of the soil. When no information about the organic carbon content was given in the literature, an average value of 2% was assumed, which is the default value in SimpleBox 3.0 (Den Hollander and Van de Meent, 2004). Finally, Appendix A1 lists the land use type present at the measurements sites, which provides information about the level of disturbance of the soil profiles.

Classification of sites

The theory applied by McKone and Bennett (2003) was originally developed for steady state soil conditions. It assumes a uniform emission of chemicals, a homogeneous soil profile and a constant rain rate. Unfortunately, hardly any validation data were available measured under such conditions, so we were compelled to include data measured in situations that did not fully fulfill the requirements of steady state conditions to obtain a substantial dataset. The total dataset was split into a group of profiles measured under (approximate) steady-state conditions, on which the theory originally applies, and a group of profiles measured in non steady-state situations, to explore the general applicability of the modeling theory. Of all measurement sites, it was evaluated if they conformed to steady-state conditions using the following criteria: 1) The soil profiles are fully undisturbed, so no agricultural activities take place. 2) Emissions or atmospheric depositions are more or less constant in time, so there is no variation in application intensity throughout a year (as is often the case for pesticides), and no abrupt change in industrial activities in the area has occurred. 3) The soil is approximately homogeneous in texture and organic carbon content. For this we assumed that both sand/silt/clay content and organic carbon content of the soils may show no larger difference than 10 volumetric percents throughout the profile. Table 3 shows to what extent the different measurement sites conform to these three criteria, and which profiles were labeled as steady state soil concentration profiles.

Chemical properties

Input data on chemical characteristics required in the model are listed in Appendix A2. Degradation rate constants were mainly derived from Howard et al. (1991). Of these data the geometric mean between the minimum and maximum value of the given half-lives was taken as input. In case of lacking data on degradation rate constants in air, soil and water, the estimation methods as proposed by Struijs and Van den Berg (1995) were used. This was the case for benzo(e)pyrene and total-PCB. In case of lacking measurement data on K_{oc}, this value was derived from the K_{ow}, following Karickhoff (1981). This was the case for citrate, oxalate, indeno(1,2,3-c,d)pyrene, total-PCB and perylene.

Profile #	*Country*	*Location*	*Criterium 1*	*Criterium 2*	*Criterium 3*	*Homogeneous profile*
			Steady-state?	*No agriculture?*	*Constant emission?*	
1-4	*Sweden*	*Nyänget, Heden*	✓	✓	–	*No*
5	*Sweden*	*Hasslöv*	✓	✓	–	*No*
6-17	*Germany*	*Hessisches Ried*	–	✓	✓	*No*
18-32	*Germany*	*Bonn*	–	–	✓	*No*
33-34	*UK*	*Park Grass*	✓	✓	✓	*Yes*
35-36	*UK*	*Broadbalk*	✓	✓	✓	*Yes*
37-38	*UK*	*Glengsaugh*	✓	✓	–	*No*
39-40	*UK*	*Hartwood*	✓	✓	–	*No*
41	*France*	*Burgundy*	–	–	✓	*No*
42	*France*	*Burgundy*	–	–	✓	*No*
43	*France*	*Burgundy*	–	–	✓	*No*
44	*France*	*Burgundy*	–	–	✓	*No*
45	*France*	*Burgundy*	–	–	✓	*No*
46	*France*	*Burgundy*	–	–	✓	*No*
47	*France*	*Burgundy*	–	–	✓	*No*
48	*Slovakia*	*Ziar*	✓	✓	–	*No*
49	*Slovakia*	*Ziar*	✓	✓	–	*No*
50	*Slovakia*	*Ziar*	✓	✓	–	*No*
51-58	*Portugal*	*Sorraia Valley*	–	–	✓	*No*
59-60	*Portugal*	*Sorraia Valley*	–	–	✓	*No*
61-63	*Germany*	*Starnberg*	✓	✓	✓	*Yes*
64-66	*Germany*	*Schauinsland*	–	✓	✓	*No*
67-75	*Denmark*	*Ejby*	✓	✓	✓	*Yes*
76-84	*Denmark*	*Sundbylille*	-	-	✓	*No*

Table 3: Compliance of the soil concentration profiles with steady-state criteria.

Fitting measured and calculated concentration profiles

From all measured concentration profiles, those were selected that show a decline of chemical concentration with depth, since the theory of Equation 5 does not suit in those situations where no declining chemical concentration with depth was measured. This was the case for four of the 84 measured profiles. For each of the measurement locations showing a declining chemical concentration with depth, a soil concentration profile was calculated following the theory described in Equation 5, in order to fit the predicted profile to the measured data points. Values for v_e and D_e were calculated as sums of advections and diffusions in the gas phase, water phase and solid phase of the soil, assuming thermodynamic equilibrium. The procedure described by McLachlan et al. (2002) was applied, using their parameterization. Next, the environmental conditions given in Appendix A1 and the physical-chemical characteristics of the compounds of Appendix A2 were used to calculate the characteristic soil penetration depth (d_p) in each situation. The values for c_o could not be calculated directly, because for none of the measurement sites emission data were available (and in some cases neither concentration values; in those cases the concentration was expressed as the fraction of the amount of chemical that was emitted). In order to enable a quantitative comparison between the calculated and the measured profiles, though, fits were made through the data points using an exponential vertical least square fitting procedure with the restriction of a fixed d_p. The natural logarithm of the measured concentration values was taken, and Equation 5 was rewritten as:

$$\ln\left(\frac{c(z)}{c_0}\right) = -\frac{z}{d_p}$$

Equation 6

Following a standard vertical least square fitting procedure, the slope of the fit is given by and the intercept ln c_o by:

$$\ln c_0 = \overline{\ln c(z)} + \frac{1}{d_p} * \bar{z}$$

Equation 7

Filling in the values for c_o and d_p in the original Equation 5, for each depth of the soil (z), the concentration $c_{(z)}$ was calculated. This procedure is further described as the 'theoretical model'.

A second fitting procedure was performed to check to what extent the derivations of the theoretical fits to the measured data was caused by setting fixed d_p-values, which might not correspond to the field situations, and to what extent the measured data points simply do or do not fit to an exponential function. A standard (empirical) regression procedure was performed on the ln values of the measured concentrations to examine the fit of the measured soil concentrations to an exponential profile. This means that both c_o and d_p were optimized to obtain a minimum sum of squares. This procedure is further described as the 'regression model'. Subsequently, a standard F-test was performed on the predictions of both fitting models to assess if

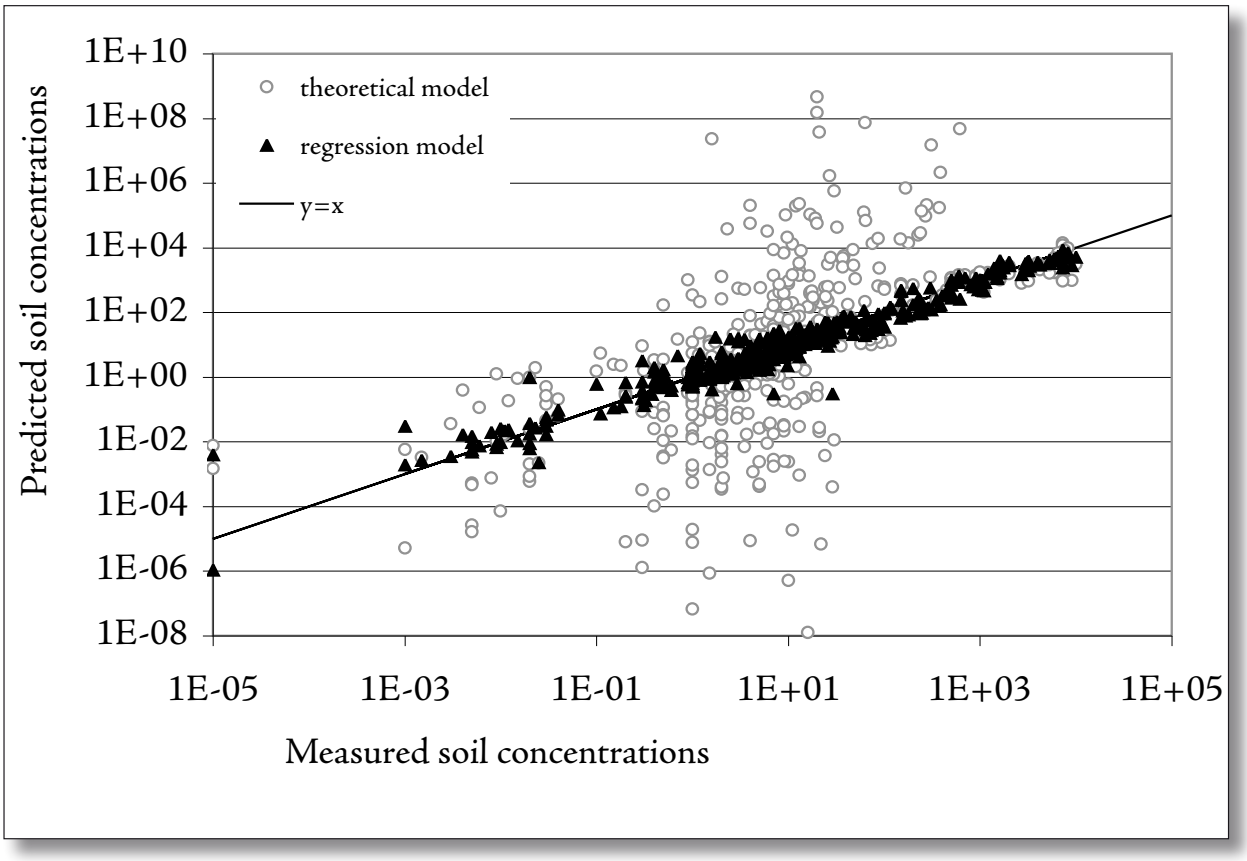

Figure 8: Calculated against measured soil concentrations of all profiles for both the regression model fit and the theoretical model fit.

one of the models yields significantly better predictions than the other.

Using both methods, fits were made for all measurement locations and the calculated concentration values were plotted against the measured concentrations. Uncertainty factors (k) of the fitted profiles were also calculated. The uncertainty factor k is defined such that 95% of the measured values are within a factor k from the median theoretical estimate (Slob, 1994), and it is based on the standard error between the calculated and measured concentration values (Huijbregts et al., 2005).

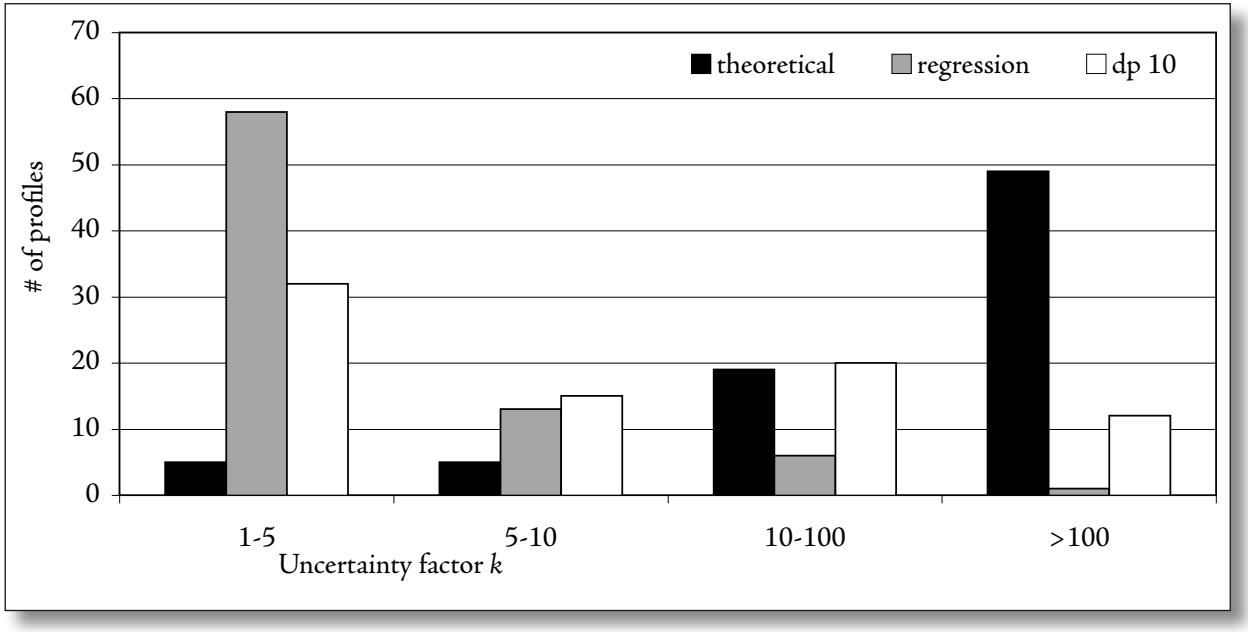

Figure 9: Numbers of profiles within the different uncertainty factor classes (k). The black bars represent the uncertainty factors following from the theoretical model fit with a fixed d_p, the grey bars represent the uncertainty factors following from the regression model fit, and the white bars represent a fitting procedure with d_p set at a value of 10 cm for all profiles.

Results and discussion

For the 80 soil profiles that show a declining concentration with depth, the theoretically expected soil penetration depths (d_p) and the values for c_o following from the two exponential fitting procedures are given in Appendix A3.

In Figure 8, the measured soil concentrations of all profiles are plotted against the calculated concentrations for both the regression model fit and the theoretical model fit (from Equation 5). It is clear that the calculated concentrations from the regression model are much closer to the measured concentration values than those of the theoretical model, which deviate up to ten orders of magnitude from the measured concentrations. From the results of the F-test it became also evident that the empirical regression model yields significantly better predictions than the theoretical model ($p < 0.001$). Figure 9 shows the distribution of the uncertainty factors (k) between the measured concentration profiles and the concentration profiles calculated based on the theoretical model fit (black bars). The median uncertainty factor of the theoreti-

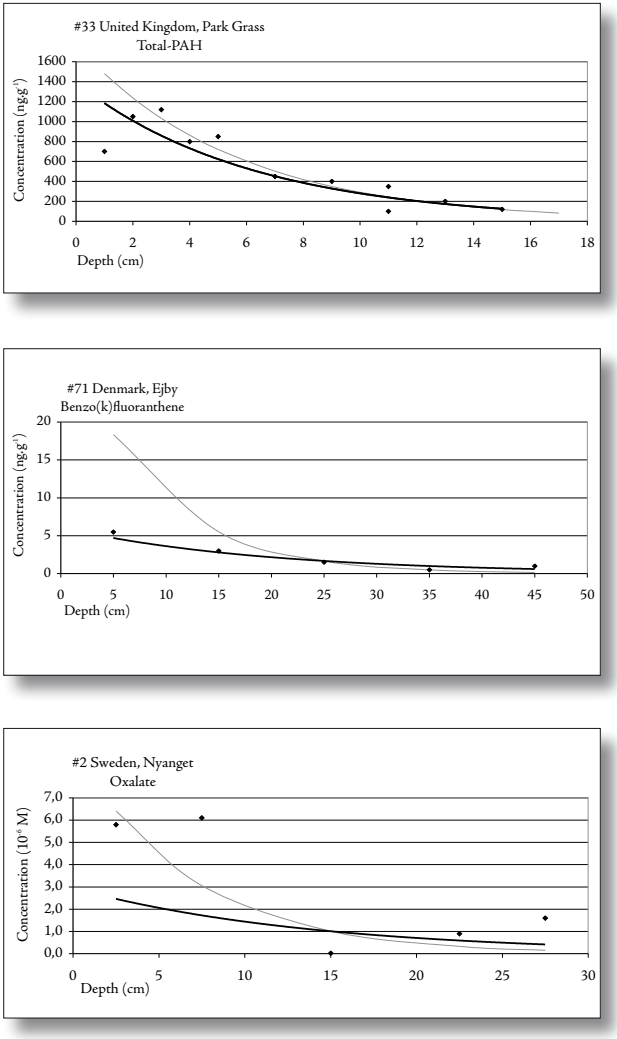

Figure 10: Examples of measured soil concentration data with theoretical fits. The grey lines represent the theoretical exponential fits with a fixed d_p, the black lines represent empirical fits without a fixed d_p. Numbers of the graphs resemble with the location numbers in Appendix A1.

cal profiles under assumed steady-state conditions is 63. The median uncertainty factor of the theoretical profiles under non steady-state conditions is 1425, while the over all median uncertainty factor has a value of 1224. In Figure 9, also the distribution of the uncertainty factors between the measured concentrations and the concentration profiles calculated based on the empirical regression model fit are plotted (grey bars). The median uncertainty factor of the empirical profiles under assumed steady-state conditions is 2.5. The median uncertainty factor of the empirical profiles under non steady-state conditions is 3.9, while the over all median uncertainty factor has a value of 3.1. The uncertainty factors of the theoretical and empirical profiles can be found in Appendix A3. From these numbers, it is clear that both the theoretical model and the regression model make much more reliable predictions about the soil concentration profiles in steady-state situations than in non steady-state situations. Of the non steady-state situations, the profiles measured in agricultural soils yield relatively high uncertainty factors. Obviously, the disturbance of the soil by ploughing activities etc. strongly influences the distribution of chemicals throughout the soil profile.

Since the regression model fit yields relatively low uncertainty factors, the assumption of chemical soil concentrations declining with depth exponentially can be considered representative in most cases, even for the non steady-state situations. This is affirmed by the fact that the situations that were considered steady-state in this study (which show the lowest uncertainty to the exponential fit) were not by definition full steady-state situations. Rain intensities were variable and soil

textures and organic carbon contents did not need to be totally homogeneous. Moreover, in some cases, it was not clear if emission intensities had been constant over a long period in time. Figure 10a and 10b show two examples from this study in which the measured concentration points fit well to an exponential profile (black lines). However, the assumption of exponentially declining soil concentrations does not always apply, particularly in situations where conditions were far from steady-state. In those situations, inhomogeneous soil textures and organic carbon contents, variable emission and precipitation intensities, and disturbances as ploughing or root-tunneling may result in chemical concentration profiles having no exponential form. This was for example the case at profile #4 (oxalate; Heden) and profile #46 (diuron; Burgundy). In Figure 10c an example is given of a soil concentration profile not declining exponentially with depth. Tables with the measured data and the theoretical exponential soil concentration profiles can be found in Appendix A4.

The uncertainty in the theoretical profiles calculated from Equation 5 can thus be explained only for a small part by the divergence from exponential profiles. The fact that the uncertainty factors of the exponential functions with a fixed d_p (theoretical model) are much higher than those without a fixed d_p (regression model) shows that the predicted values of d_p do not always correspond to reality. In the theoretical model, the predicted value of d_p is often too low, which results in an overestimation of the values for c_o. This was the case in 45% of the cases. On average, the value of d_p for these profiles was underestimated by a factor of 11. It appeared that no relationships exist of the divergence between measured and predicted d_p-values with different physical-chemical properties of the studied compounds, or with land use or other environmental parameters. In Figure 10a an example is given of an exponential fit with a fixed d_p in which the predicted d_p appears to be in the correct range (grey line). Figure 10b shows an example of a fit in which the exponential fit without a fixed d_p is good (black line), but where the restriction of a theoretically estimated d_p results in a high c_o and a soil profile not corresponding to reality (grey line). In Figure 11, all predicted values for d_p from the theoretical model of Equation 5 are plotted against the d_p-values derived from the regression model fit. This figure shows that more than 90% of the theoretically predicted d_p-values are within a range of 0-10 cm, while the range of d_p-values derived from the regres-

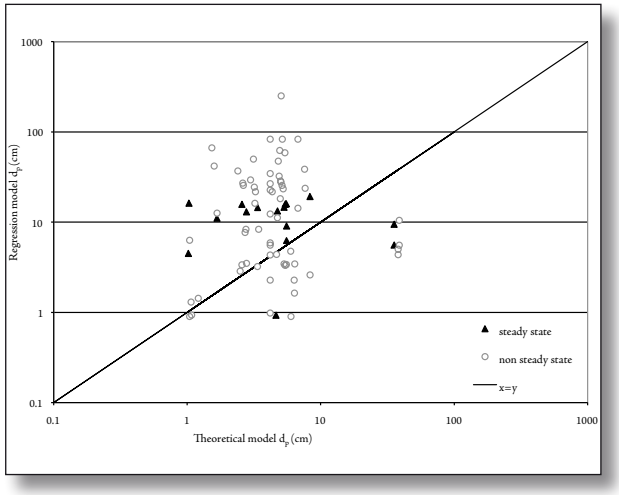

Figure 11: Predicted values for d_p from the theoretical model fit of Equation 5 plotted against the d_p-values derived from the regression fit for both steady-state and non steady-state concentration profiles.

sion model fit is much larger. Obviously, the theoretical model is not capable of describing the total actual variation in d_p-values under different environmental conditions and for different compound types. Besides, most theoretically predicted d_p-values are lower than the d_p-values from the regression fit. The consequence of underestimating the value for d_p and thus overestimating the value for c_o is that substance flows from the soil surface towards the air and the surface water are predicted unrealistically high.

One possible cause of unrealistic predictions of d_p is the uncertainty in the physical-chemical properties of the compounds studied. Particularly, degradation rate constants, for which the model is rather sensitive, are often highly uncertain (Aronson et al., 2006; Hertwich et al., 1999). Second, the assumption of constant coefficients for degradation, diffusion and advection throughout the soil profile may not correspond to reality, especially in situations where inhomogeneous soil profiles are apparent. Particularly for compounds with a long half-life in soils, degradation rates may be relatively high in the top soil layer with regard to deeper soil regions. Neglecting these differences can lead to relatively high concentration predictions in the upper part of the soil. Third, we neglect the process of chemicals in groundwater migrating upward into the overlying soils. For certain chemicals and environmental systems, this process can have a significant influence on the soil concentrations (e.g. Ashworth and Shaw, 2006). Similarly, tillage activities on agricultural soils are not incorporated in the estimated of D_e. Finally, a parameter leading to biased predictions of d_p is the factor representing bioturbation, cryoturbation and erosion into cracks, which is incorporated in the calculation of D_e. Cousins et al. (1999) and McLachlan et al. (2002), who summarized these processes in one vertical sorbed phase diffusion coefficient, already showed that this factor can have a substantial influence on soil concentrations. However, McLachlan et al. (2002) also concluded that there is a considerable variability in the value of the vertical sorbed phase diffusion coefficient between soils. It would therefore be recommended to take into account the local factors influencing this coefficient in calculating a representative value of d_p. If this results in a more realistic prediction of d_p, the theoretical model for calculating exponential soil concentration profiles will probably render more satisfying results.

For most modeling purposes, however, no detailed local information is available on soil properties, environmental conditions and turbation processes. Though, also in those situations, taking into account exponentially declining soil concentration profiles in the modeling calculations is recommended. From our validation data it appears that, for this group of compounds, using a standard value for the soil penetration depth (d_p) of about 10 cm yields reliable estimates of the soil concentration profiles (the median d_p-value derived from the regression model fit is 12.4 cm). Figure 9 shows the distribution of the uncertainty factors (k) between the measured concentration profiles and the concentration profiles calculated based on the fit with a d_p-value of 10 cm (white bars). The median uncertainty factor of the profiles under assumed steady-state conditions is 3.6, while the median uncertainty factor of the profiles under non steady-state conditions is 9.9.

These relatively low uncertainty factors indicate a reliable model that will yield better estimates of chemical fluxes out of the soil than models that base their estimations on average soil concentrations. It should be noted, however, that the group of compounds studied here consists almost fully of hydrophobic chemicals with a log K_{ow} > 3. This implies that the default d_p of 10 cm is recommended for these types of compounds only.

Over all, the reliability of e.g. multimedia fate model predictions will improve when taking into account depth dependent soil concentrations as proposed in Equation 5, the d_p-values estimated either based on local environmental conditions or on a fixed value of d_p, particularly in undisturbed soils where approximate steady-state conditions are present. Since information on local environmental conditions is often lacking, and since no model formulation has been proposed yet that includes these local factors, for now, we recommend the use of a constant d_p-value of 10 cm as an optimal screening model solution for compounds with log K_{ow} > 3.

Conclusion

Chemical concentrations in soils can be assumed to decline with depth exponentially, particularly in relatively undisturbed soil profiles. In half of the soil profiles included in this study, the theoretical model of Equation 5 predicts values for d_p in the right order of magnitude, while in 45% of the cases, d_p is significantly underestimated. More realistic predictions of d_p may be obtained by incorporating location specific chemical properties and vertical sorbed phase diffusion coefficients. For now, we recommend the use of a constant d_p-value of 10 cm as an optimal screening model solution for compounds with log K_{ow} > 3. The relatively simple theory validated in this study can be an enrichment for different modeling purposes. For example in generic multimedia fate models assuming homogeneous chemical concentrations throughout a soil profile or in local scale plant uptake models, since the chemical concentration profiles predicted by this theory give a more realistic representation of chemical distributions in soils and of the substance flows out of soils than homogeneous models do.

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4 BasinBox: a generic multimedia fate model for predicting the fate of chemicals in river catchments

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Abstract

Multimedia fate models have proven to be very useful tools in chemical risk assessment and management. This paper presents BasinBox, a newly developed steady-state generic multimedia fate model for evaluating risks of new and existing chemicals in river basins. The model concepts, as well as the intermedia processes quantified in the model, are outlined, and an overview of the required input parameters is given. To test the BasinBox model, calculations were carried out for predicting the fate of chemicals in the river Rhine basin. This was done for a set of 3175 hypothetical chemicals and three emission scenarios to air, river water and cropland soils. For each of these hypothetical chemicals and emission scenarios the concentration ratio between the downstream area and the upstream area was calculated for all compartments. From these calculations it appeared that BasinBox predicts significant concentration differences between upstream and downstream areas of the Rhine river basin for certain types of chemicals and emission scenarios. There is a clear trend of increasing chemical concentrations in downstream direction of the river basin. The calculations show that taking into account spatial variability between upstream, midstream and downstream areas of large river basins can be useful in the predictions of environmental concentrations by multimedia fate models.

Introduction

For more than twenty years now, multimedia fate models have been used for the prediction of chemical fate and exposure in the environment. Baughman and Lassiter (1978) and Mackay and Paterson (1981) first introduced this kind of models, the so-called 'fugacity models' or 'box models', in which the fate of chemicals in different environmental media was calculated based on physical-chemical properties of the compound, environmental characteristics and emission data. The first models, e.g. Mackay's unit world model (Mackay and Paterson, 1981; Mackay et al., 1983), were relatively simple in structure and detail, but over time the models became more complex and sophisticated. Different types of compartments were added to the models, i.e. vegetation compartments (Trapp and Matthies, 1996; Severinsen and Jager, 1998; Cousins and Mackay, 2001), and organic film-compartments coating impervious surfaces (Diamond et al., 2001). Nested, dynamic and GIS-based models were developed (Brandes et al., 1996; Woodfine et al., 2001; Suzuki et al., 2004), models with layered air and soil compartments arose (McKone, 1993; Toose et al., 2004), and models for multi-species chemicals were introduced (Fenner et al., 2000; Cahill and Mackay, 2003).

Multimedia fate models have proven to be very useful tools in chemical risk assessment and management. Their multimedia character and relatively low complexity make them particularly useful to evaluate the fate of new and existing chemicals. In the European Union the EUSES model (Vermeire et al., 1997; Vermeire et al., 2005) is currently being used for risk assessment and management purposes, while in the USA, the Total Risk Integrated Methodology (TRIM.FaTE; US-EPA, 2002) is typically applied. Most multimedia fate models used in the risk assessment of chemicals are based on a geo-political parameterization, e.g. per country or province, and originate from a generic environmental approach, as for example described in the EU Technical Guidance Documents (ECB, 2003). For water quality management purposes in the European Union, however, the regulatory concept is shifting more and more towards an environmentally specific approach. This regulatory concept is described in the European Water Framework Directive (EC, 2000), in which the European Union defined ecological and chemical water standards at a catchment scale. This catchment approach could also be very advantageous for the risk assessment policy of new and existing chemicals, since river basins form more clearly defined physical entities than political regions. Except for air-borne transport, transport of chemicals occurs only within the basin, which facilitates the description of transport flows in the model. Moreover, in the case of river basin modeling, floodplain areas, which are being regarded as valuable areas for nature conservation, can be modeled separately. It will therefore be useful to implement the concept of catchment based modeling in the process of risk management of chemicals.

Very few multimedia fate models have been developed using river catchments as the basic environmental unit, since chemical modeling in catchments usually focuses on in-stream water quality only. This, for example, is the case in the Great-ER model (Feijtel et al., 1997)

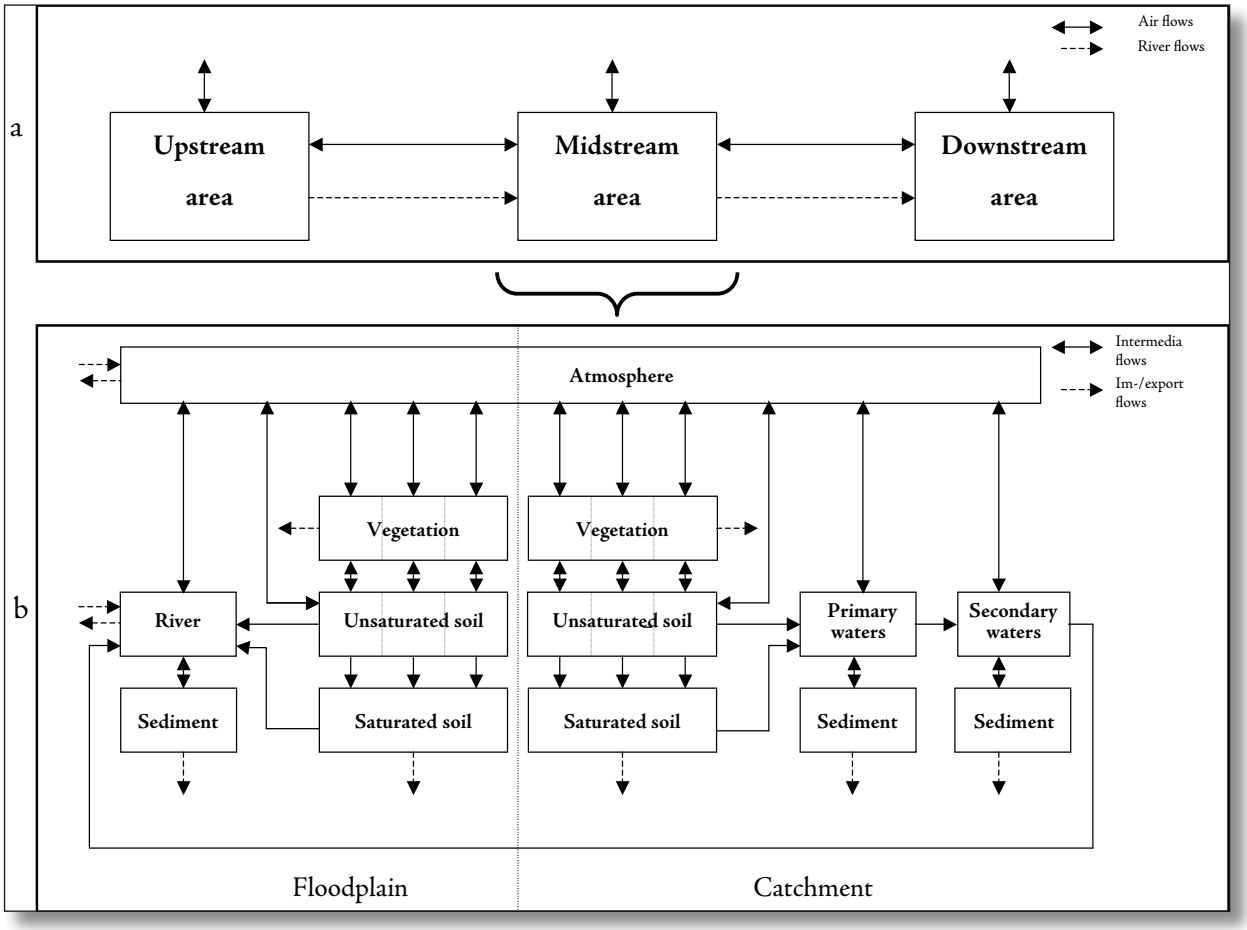
and the LOIS model (Boorman, 2003). Coulibaly et al. (2004) did develop a multimedia catchment model for the Passaic River Watershed in the USA, and Suzuki et al. (2004) described a multimedia model built up from 38,000 river catchments in Japan (G-CIEMS), but both are very site-specific GIS-based models of relatively small basins (up to 200 km^2) that can not be easily applied to other river catchments. The goal of this study is to develop a generic steady-state multimedia fate model to evaluate risks of new and existing chemicals in river basins. Here, this model, called BasinBox, is presented. The model concept, as well as the environmental processes considered in the model are outlined, and an overview of the required input parameters is given. Furthermore, the model is applied in a case study on the river Rhine basin area for a set of 3175 hypothetical chemicals, representing the whole range of chemical property combinations, to test whether the catchment approach applied in BasinBox yields valuable insights in the context of multimedia fate modeling. For that purpose, concentration ratios between the upstream area and the downstream area are analyzed for various compartments and emission scenarios.

Materials and methods

Model description

In the BasinBox model, the river basin is subdivided into an upstream, midstream and downstream area, following Schumm's (1977) idealized scheme of a river basin consisting of three zones arranged in downstream sequence. Since many environmental parameters and process intensities vary between the different zones of a river basin, this subdivision allows the modeller to incorporate basic spatial variability into the model. The three model areas are interconnected by single-direction river flows and two-direction air flows. Figure 12a gives a schematic representation of the three sequential areas and the connections between these areas.

Each of the upstream, midstream and downstream areas consists of twenty-one compartments, representing different environmental media. Nine of these compartments belong to the floodplain zone and eleven compartments belong to the catchment zone. One single air compartment covers both the floodplain and the catchment zone. The floodplain zone is defined as the area of the river basin that consists of the river or its main tributaries and the land that is being flooded temporally each year. We chose to make the distinction between the floodplain and the catchment zone since some processes, like sedimentation and groundwater flow, proceed differently in these two zones. Moreover, floodplain areas are regarded as valuable habitats for nature conservation and development (Nienhuis et al., 2002; ECNC, 2004; De Nooij et al., 2006). In the floodplain zone, a river and a sediment compartment, three unsaturated soil compartments (pasture-, cropland- and natural soil), saturated soil, and three vegetation compartments (pasture-, cropland-, and natural vegetation) have been distinguished. In the catchment zone one can find compartments for primary waters, secondary/tertiary waters and sediment, three unsaturated soil compartments (pasture-, cropland- and other soil), saturated soil, and three



vegetation compartments (pasture-, cropland-, and natural vegetation). A schematic representation of the compartmental construction and the transport routes between the compartments is given in Figure 12b.

The concentrations calculated by BasinBox are affected by emissions, degradation processes and processes that cause chemical mass flows to and from the com-

Figure 12: Schematic representation of the BasinBox model. 12a (upper): schematic representation of the three sequential areas (up-, mid- and downstream) and the connections between these areas. 12b (lower): schematic representation of the compartmental construction and the transport routes between the compartments.

partments. Mass balance equations can be written for all compartments, having the following general format:

$$V_i * \frac{\partial C_i}{\partial t} = Emission_i + Import_i - Export_i - Degradation_i + Advection_{ij} + Diffusion_{ij}$$

Equation 8

with V_i being the volume of compartment i (m^3) and C_i being the chemical concentration in that compartment ($mol.m^{-3}$). $Emission_i$, and $Degradation_i$ represent emission to, and degradation from compartment i, respectively. $Import_i$ is the mass flow to compartment i from outside the basin area, while $Export_i$ stands for the mass flow from i out of the basin area. $Advection_{ij}$ and $Diffusion_{ij}$ are the gross advective and diffusive mass flows between compartment i and j within the river basin. At steady state, the mass flows balance. The set of mass balances is solved using a matrix inversion routine. BasinBox calculates concentrations of chemicals in each of the compartments, using Microsoft Excel® software in combination with the Poptools-extension (CSIRO, 1994).

Since BasinBox is a steady state model, it is assumed that the environmental properties of and emissions to the compartments do not change over time. It is also assumed that equilibrium exists between the different phases within each compartment (e.g. gas, water and solids in soil). Moreover, each compartment is assumed to be completely mixed, which implies that all environmental properties and concentrations are equal throughout a compartment. Exceptions to this are the unsaturated soil compartments, where depth-dependent concentration differences in soil can significantly affect substance flows (e.g. volatilization, leaching) throughout the soil profile. To overcome this problem, the theoretical principle of exponentially declining soil concentrations with depth of McKone & Bennett (2003), as implemented in multimedia models by Hollander et al. (2004), was introduced in the BasinBox model. This method applies correction factors that account for the deviation of depth-dependent soil concentrations from depth-averaged concentrations.

Model processes

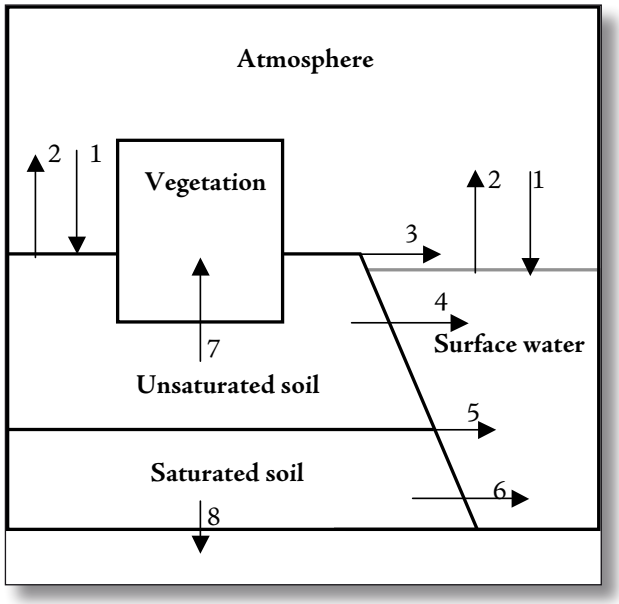
All intermedia mass flows affecting the concentration of a chemical in a compartment (in $mol.s^{-1}$) can be described as the product of a transport coefficient (in $m^3.s^{-1}$) and the concentration (in $mol.m^{-3}$) in the compartment from which the mass flow originates. The transport coefficient is calculated as the product of a mass transfer coefficient (in $m.s^{-1}$) and the interfacial area (in m^2). We distinguish diffusive and advective mass flows and transport coefficients. A diffusive mass flow is treated as a process driven by differences in the chemical potentials in the two media. Advective mass flows proceed by a carrier that physically flows from one compartment to another, e.g. by air or water. The amount of advective mass transport depends on the rate of the carrier flow and the concentration of the compound in the carrier.

Air and water transport flows

In the BasinBox model, air and water are regarded as the main carriers for advective mass flows. Air transport within the modeled river basin as well as into and out of it is dependent on the wind direction and the geometric orientation of the areas in the river basin, e.g. the position of the upstream area with regard to the midstream area, and the position of the midstream area with regard to the downstream area. To calculate the source of imported air, and subsequently, the chemical concentration in the air imported to the area, for each of the possible combinations of wind directions and orientations of the river basin, an air-inflow scenario was formulated for the upstream, midstream and downstream area. This generic calculation method enables the user to enter all possible orientations of a river basin to calculate the source of airflows into and out of the upstream, midstream and downstream area. As constant atmospheric pressure is assumed, the amount of imported air equals the amount of exported air. This amount is estimated based on the residence time of air in the upstream, midstream and downstream area, calculated using the annual average wind speed, the distance across the area in each of the eight compass directions, and the frequencies of wind directions, following the method described by Webster et al. (2004).

Since there is no water flow over the borders of a river catchment, it is possible to accurately construct a water balance, describing all relevant water transport processes within a river basin (Figure 13). Figure 13a shows the water transport routes between air and soil, air and water, soil and water and soil and vegetation. Water enters the model as precipitation, of which a certain fraction evaporates. A fraction of the water runs off over the soil surface to one of the surface water compartments, another fraction is discharged as subsurface flow at the mechanical reworking depth, and a third fraction is drained by tube drainage (except in natural soils where no tube drainage is assumed). The remaining water percolates to the saturated soil compartments. In the catchment zone of the model, it is assumed that a certain amount of groundwater is exported from the saturated soil zone to deeper aquifers and thus exported from the system. The remainder is transported from the saturated soil zone to the surface water compartments. In the floodplain zone all groundwater is assumed to recharge to the surface water compartment, since no groundwater export takes place at a location so close to the drainage base of the system.

Figure 13b shows the water transport routes between the different surface water compartments. The primary water compartments (ditches, pools) of the up-, mid- and downstream areas discharge to the secondary and tertiary water compartments (canals, brooks, small rivers) of these areas and those again discharge to their river water compartments. In the river compartments, water is being discharged in a downstream direction. A constant volume of the surface water compartments is assumed; this means that all surplus water is being transported following the routes described in Figure 13b. From the downstream area river compartment, water is exported from the system at the river mouth.



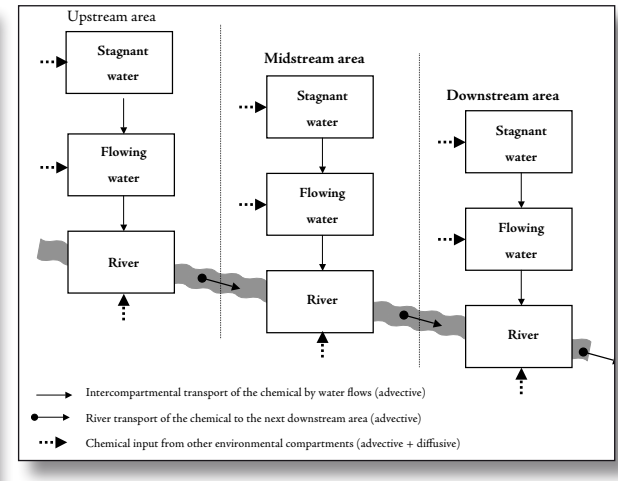


Figure 13b: Water flows between the different surface water compartments.

Figure 13: Schematic representation of the water balance elements of BasinBox. Figure 13a: Water flows between the air, soil, surface water and vegetation compartments. 1 = rain input (to soil and water), 2 = evaporation, 3 = surface runoff, 4 = subsurface runoff, 5 = tube drainage, 6 = groundwater drainage, 7 = transpiration, 8 = groundwater discharge to deeper aquifers.

Intermedia chemical transport processes

Air-surface area exchange

Advective air-unsaturated soil and air-water transport occurs by wet and dry deposition. For the calculation of the dry deposition chemical mass flow, the dry deposition velocity of aerosol particles and the fraction of chemicals associated with aerosol in the atmosphere are used (Brandes et al., 1996). An interception fraction for dry aerosol interception by vegetation is introduced. Wet deposition is divided into gas washout and aerosol washout processes, both dependent on rain intensity and the fraction of gas and aerosols in the atmosphere. Gas washout is calculated using the dimensionless air-water partition coefficient (Den Hollander et al., 2004), while aerosol washout is calculated based on the aerosol collection efficiency (Mackay, 1991). For aerosol washout an interception fraction for vegetation is inserted. It is assumed that vegetation causes no interception in the case of gas washout.

Diffusive air-water, air-soil and air-vegetation transport occurs by gas absorption and volatilization. These processes are calculated using the classic two-film resistance model (Schwarzenbach et al., 1993). For the soil-air mass flows a correction factor accounting for

the deviation of the concentration at the top of the soil compartment from the average soil concentration (Hollander et al., 2004) is inserted. Diffusive air to vegetation transport vice versa is estimated from the overall mass transfer coefficient at the air-plant interface for natural and agricultural vegetation, following the description of Severinsen and Jager (1998).

Water-sediment exchange and sediment burial

Advective transport between the water and the sediment compartments occurs by sedimentation and resuspension. Gross sedimentation rates are calculated from the settling velocity of suspended particles and the concentration of suspended matter in the water compartments following the method of Brandes et al. (1996). Net sedimentation rates in the up-, mid- and downstream areas were derived from literature (Schwarzenbach et al., 1993; Trapp, 1996; Hofstee and Leenaers, 2002). Resuspension rates equal the difference between the gross sedimentation rates and the net sedimentation rates. Diffusive exchange proceeds by adsorption and desorption processes, based on the partial mass transfer coefficients at the water and the sediment side of the water-sediment interface. In the BasinBox model, the sediment compartments are modeled with a fixed depth. Therefore, a sediment burial flow is introduced, the burial mass transfer coefficient being equal to the product of the net sedimentation rate and the interfacial area.

Unsaturated soil-vegetation exchange

Chemical transport from unsaturated soil to vegetation proceeds by an advective transpiration flow. Severinsen and Jager (1998) described the method used here, using a transpiration stream concentration factor (Briggs et al., 1982). Litter flow causes chemical transport from the vegetation compartments to the unsaturated soil compartments, of which the amount is derived from the growth rate of vegetation, and the harvesting efficiency (Severinsen and Jager, 1998).

Unsaturated soil-saturated soil-surface water exchange

Several advective water-bound soil to water processes are modeled. On agricultural pasture and cropland soils, one water flow occurs at the soil surface (surface runoff), one at the mechanical reworking depth (subsurface flow), and one at the typical depth of drainage tubes (tube drainage). For natural soils, only surface runoff and subsurface flow processes are modeled. The principle of depth-dependent chemical concentrations is used for calculating the amount of chemicals involved in the different processes. For the surface runoff calculation, both the process of solute transport in runoff water and erosion (Asselman, 1997) are modeled. The fraction of precipitation that does not flow from the unsaturated soil compartments to the surface water compartments percolates to the saturated soil zone. The chemical amount that is transported from the saturated soil zone to deeper aquifers is determined by an export fraction derived from literature (De Wit, 1999), the remainder is recharged to the surface water compartments.

Degradation

All chemical degradation is assumed to obey (pseudo) first order kinetics, following from a degradation rate constant, the volume of the compartment and the con-

centration. Following the method of Den Hollander et al. (2004), the degradation rate constant in air is estimated from the fraction of the chemical in air that is associated with aerosol particles, and the OH-radical concentration in air. Values for the degradation rate constants in water, sediments and soils are calculated using the degradation rate constant in the dissolved phase, the bulk degradation rate constant in sediments and in soils respectively, corrected for the actual temperature. The chemical degradation constants in vegetation are assumed to be ten times higher than those in soil (Brandes et al., 1996).

Model parameterization

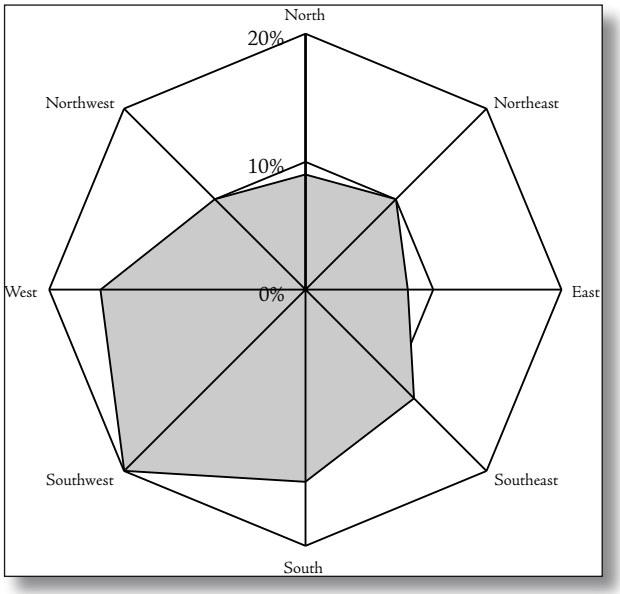
The input for BasinBox consists of physical-chemical properties of the compound studied, environmental characteristics and emission data, the latter two being user-defined. Required physical-chemical properties of the compound are its molecular weight, octanol-water partition coefficient (K_{ow}), vapour pressure, solubility, melting point, and degradation rate constants for bulk sediment, bulk soil, and the gas phase. The vapour pressure, the solubility and the degradation rates of a chemical are modeled as temperature dependent variables. Using the physical-chemical data the model estimates intermedia partition coefficients. The air-water partition coefficient is estimated from the ratio of the vapour pressure and the water solubility of the compound. The air-aerosol partitioning is determined on the basis of the chemical's vapour pressure, according to Junge (1977). The solids-water partition coefficient is calculated based on the relationship with K_{ow} and the organic carbon content of the soil proposed by DiToro et al. (1991). The bioconcentration factor is estimated from the K_{ow} and the fat content of the biota. For vegetation, the concentration ratio between plant tissue and water in thermodynamic equilibrium is estimated from the water and lipid contents of the plant tissue (Severinsen and Jager, 1998).

Values for the environmental parameters and the emission rates are, dependent on the model scenario, to be defined by the user. The environmental parameters that need to be entered in the BasinBox model are listed in Table 4. Emissions in the model can take place to the air compartment, the water compartments and the different soil compartments.

Case study for the river Rhine basin

Model area

To test the BasinBox model, example calculations were carried out for predicting the fate of chemicals in the river Rhine basin. Environmental input parameters for BasinBox were collected for the upstream, midstream, and downstream areas of the Rhine basin (Table 4). The geometrical orientation of the upstream area with regard to the midstream area of the Rhine basin is South, while the orientation of the midstream area with regard to the downstream area is Southeast. Based on this orientation, together with information on the percentages of wind flowing in from the different compass directions, the chemical concentration in the inflowing air in the different areas of the river Rhine basin was calculated (Figure 14). Figure 14a and Table 4 show the percentage of wind directions occurring in the river Rhine basin. For each of the



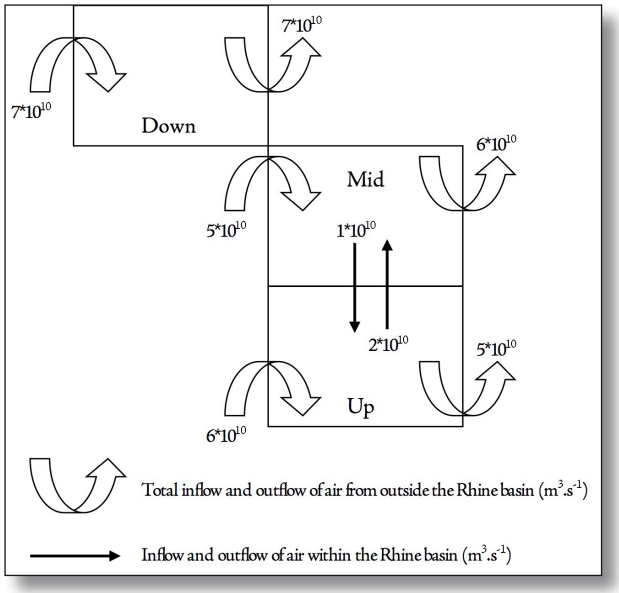


Figure 14: Schematic representation of the calculation of the chemical concentration in the inflowing air in the different areas of the river Rhine basin. 14a (left): The percentage of each of the wind directions occurring in the river Rhine basin (KNMI, 2004). 14b (right): Total amounts of inflowing and outflowing air in the different areas of the Rhine basin..

wind directions, the model estimates the fraction of inflowing air occurring from outside the river basin as well as the fraction of inflowing air taking place from the other areas within the basin. Figure 14b shows the total amounts of inflowing and outflowing air in the different areas of the Rhine basin, calculated using the wind directions of Figure 14a and the residence times of air in the different areas.

In BasinBox it is possible to model periodical inundations of the floodplain zone of the river basin. For the Rhine basin, a yearly inundation of four weeks is assumed in the downstream area of the basin (Hofstee and Leenaers, 2002). During this period gross and net sedimentation rates from the river water to the inundated floodplain soil are assumed to equal those rates from the river water to the sediment compartment. For the upstream and midstream areas of the Rhine basin, no periodical flooding was assumed in this case study.

Set of hypothetical chemicals

For the example calculations, a set of 3175 hypothetical chemicals was used, covering the entire space of plausible chemical partitioning properties and half-lives. The advantage of using this set instead of real chemical data is that even a set of hundreds of real chemicals does not densely cover the space of possible chemical property combinations (Fenner et al., 2005). The set of hypothetical chemicals used here includes all possible combinations of integer values of log K_{aw} from –11 to 2 and log K_{ow} from –1 to 8 with the restriction that $-1 \leq (\log K_{ow} - \log K_{aw}) \leq 15$ (Fenner et al., 2005). For the degradation half-lives, all possible combinations of half-lives in air of 4, 24, 168, 1000, and 8760 h with half-lives in water of 24, 168, 1000, 8760, and 87,600 h were used. The half-life in soil and sediment was set to twice the half-life in water, in order to limit the chemical properties that were varied to four (Stroebe et al., 2004).

Emission scenarios

With the whole set of hypothetical chemicals, the BasinBox model was run for three emissions, towards air, river water and cropland soils. Emission input towards air and river water was estimated using population density numbers, following Prevedouros et al. (2004). This method assumes that chemicals emitted to air and river water are mainly released from densely populated urban areas. Based on population density numbers in the Rhine basin area (Table 4), air and river water emissions take place in a ratio of 1 : 1.2 : 2 between the upstream, midstream and downstream areas (Nationmaster, 2005). Diffuse emissions to cropland soils will typically be pesticides, so input to cropland soils was estimated based on differences in cropland area between the upstream, midstream and downstream areas as well as on differences in the typical pesticide emission dose between the different areas (Table 4). According to this method, the emission ratio between the upstream, midstream and downstream areas in the Rhine basin area is 1 : 2.6 : 6.3 for the floodplain soil compartment, and 1 : 1.9 : 4.5 for the catchment soil compartment (FAO, 2001; Nationmaster, 2005). Since we were interested in concentration differences between the upstream, midstream and downstream areas, rather than in absolute concentrations, only relative emission rates were required for the calculations.

Concentration ratios

For all hypothetical chemicals, the concentration ratio between the upstream area and the downstream area was calculated for each emission scenario and for all compartment types. These results were analysed in order to select all combinations of chemical properties for which the concentration ratio between the downstream and upstream areas is larger than 100, respectively 10 or smaller than 0.01, respectively 0.1. This was done to select those chemicals for which predicting concentrations within the river Rhine area for the upstream, midstream and downstream area separately can be relevant. For all combinations of emission scenario and compartment type at which concentration ratios >100 or <0.01 occur, series of chemical space plots were created. In these chemical space plots, the concentration ratio between downstream and upstream areas is plotted against K_{ow} and K_{aw} for a certain value of the chemical degradation

Environmental parameter	*Unit*	*Value up-stream*	*Value mid-stream*	*Value down-stream*	*Reference*
Total area	*[m²]*	*6.17 x 10¹⁰*	*6.17 x 10¹⁰*	*6.17 x 10¹⁰*	*-*
Area fraction river	*[-]*	*1.00 x 10⁻⁰³*	*1.62 x 10⁻⁰³*	*1.88 x 10⁻⁰³*	*a*
Area fraction pasture soil floodplain	*[-]*	*1.52 x 10⁻⁰³*	*1.29 x 10⁻⁰³*	*2.15 x 10⁻⁰³*	*a*
Area fraction cropland soil floodplain	*[-]*	*4.40 x 10⁻⁰⁴*	*1.38 x 10⁻⁰³*	*1.05 x 10⁻⁰³*	*a*
Area fraction other soil floodplain	*[-]*	*2.05 x 10⁻⁰³*	*1.64 x 10⁻⁰³*	*5.65 x 10⁻⁰⁴*	*a*
Area fraction pasture soil catchment	*[-]*	*3.64 x 10⁻⁰¹*	*2.92 x 10⁻⁰¹*	*4.68 x 10⁻⁰¹*	*a*
Area fraction cropland soil catchment	*[-]*	*1.06 x 10⁻⁰¹*	*3.12 x 10⁻⁰³*	*2.30 x 10⁻⁰¹*	*a*
Area fraction other soil catchment	*[-]*	*4.89 x 10⁻⁰¹*	*3.70 x 10⁻⁰³*	*1.23 x 10⁻⁰¹*	*a*
Area fraction primary waters catchment	*[-]*	*2.59 x 10⁻⁰²*	*4.72 x 10⁻⁰⁴*	*8.71 x 10⁻⁰²*	*a*
Area fraction secondary waters catchment	*[-]*	*1.00 x 10⁻⁰²*	*1.99 x 10⁻⁰²*	*8.71 x 10⁻⁰²*	*a*
Mixed height air compartment	*[m]*	*1.00 x 10⁰³*	*1.00 x 10⁰³*	*1.00 x 10⁰³*	*b*
Depth river compartment	*[m]*	*3.00 x 10⁰⁰*	*3.00 x 10⁰⁰*	*5.00 x 10⁰⁰*	*c*
Depth sediment compartments	*[m]*	*3.00 x 10⁻⁰³*	*3.00 x 10⁻⁰³*	*3.00 x 10⁻⁰³*	*b*
Depth primary waters compartment	*[m]*	*1.00 x 10⁰⁰*	*1.00 x 10⁰⁰*	*1.00 x 10⁰⁰*	*d*
Depth secondary waters compartment	*[m]*	*2.00 x 10⁰⁰*	*2.00 x 10⁰⁰*	*2.00 x 10⁰⁰*	*-*
Depth unsaturated soil compartments	*[m]*	*1.00 x 10⁰⁰*	*1.00 x 10⁰⁰*	*1.00 x 10⁰⁰*	*e*
Depth saturated soil compartments	*[m]*	*2.00 x 10⁰⁰*	*2.00 x 10⁰⁰*	*2.00 x 10⁰⁰*	*-*
Solid phase advection velocity soil	*[m.s⁻¹]*	*6.34 x 10⁻¹²*	*6.34 x 10⁻¹²*	*6.34 x 10⁻¹²*	*b*
Solid phase turbation coefficient soil	*[m.s⁻¹]*	*6.37 x 10⁻¹²*	*6.37 x 10⁻¹²*	*6.37 x 10⁻¹²*	*b*
Volume fraction solids soil	*[-]*	*6.00 x 10⁻⁰¹*	*6.00 x 10⁻⁰¹*	*6.00 x 10⁻⁰¹*	*-*
Volume fraction water unsaturated soil	*[-]*	*2.00 x 10⁻⁰¹*	*2.00 x 10⁻⁰¹*	*2.00 x 10⁻⁰¹*	*-*
Volume fraction air unsaturated soil	*[-]*	*2.00 x 10⁻⁰¹*	*2.00 x 10⁻⁰¹*	*2.00 x 10⁻⁰¹*	*-*
Volume fraction water saturated soil	*[-]*	*4.00 x 10⁻⁰¹*	*4.00 x 10⁻⁰¹*	*4.00 x 10⁻⁰¹*	*-*
Volume fraction water sediment	*[-]*	*8.00 x 10⁻⁰¹*	*8.00 x 10⁻⁰¹*	*8.00 x 10⁻⁰¹*	*f*
Volume fraction solids sediment	*[-]*	*2.00 x 10⁻⁰¹*	*2.00 x 10⁻⁰¹*	*2.00 x 10⁻⁰¹*	*f*
Volume fraction water vegetation	*[-]*	*8.00 x 10⁻⁰¹*	*8.00 x 10⁻⁰¹*	*8.00 x 10⁻⁰¹*	*b*
Mass fraction lipids vegetation	*[-]*	*1.50 x 10⁻⁰²*	*1.50 x 10⁻⁰²*	*1.50 x 10⁻⁰²*	*b*
Leaf area index pasture vegetation	*[m².m⁻²]*	*5.06 x 10⁰⁰*	*5.06 x 10⁰⁰*	*5.06 x 10⁰⁰*	*g*
Leaf area index cropland vegetation	*[m².m⁻²]*	*1.71 x 10⁰⁰*	*1.71 x 10⁰⁰*	*1.71 x 10⁰⁰*	*g*

Environmental parameter	*Unit*	*Value up-stream*	*Value mid-stream*	*Value down-stream*	*Reference*
Leaf area index natural vegetation	*[m².m⁻²]*	*3.62 x 10⁰⁰*	*3.62 x 10⁰⁰*	*3.62 x 10⁰⁰*	*g*
Vegetation cover pasture vegetation	*[-]*	*7.10 x 10⁻⁰¹*	*7.10 x 10⁻⁰¹*	*7.10 x 10⁻⁰¹*	*h*
Vegetation cover cropland vegetation	*[-]*	*8.60 x 10⁻⁰¹*	*8.60 x 10⁻⁰¹*	*8.60 x 10⁻⁰¹*	*h*
Vegetation cover natural vegetation	*[-]*	*9.00 x 10⁻⁰¹*	*9.00 x 10⁻⁰¹*	*9.00 x 10⁻⁰¹*	*h*
Vegetation mass pasture vegetation	*[kg.m⁻²]*	*1.20 x 10⁰⁰*	*1.20 x 10⁰⁰*	*1.20 x 10⁰⁰*	*i*
Vegetation mass cropland vegetation	*[kg.m⁻²]*	*1.80 x 10⁰⁰*	*1.80 x 10⁰⁰*	*1.80 x 10⁰⁰*	*i*
Vegetation mass other vegetation	*[kg.m⁻²]*	*2.40 x 10⁰⁰*	*2.40 x 10⁰⁰*	*2.40 x 10⁰⁰*	*i*
Wet density of vegetation	*[kg.m⁻³]*	*9.00 x 10⁰²*	*9.00 x 10⁰²*	*9.00 x 10⁰²*	*i*
Average wind speed	*[m.s⁻¹]*	*2.90 x 10⁰⁰*	*2.90 x 10⁰⁰*	*2.90 x 10⁰⁰*	*j*
Fraction of wind from direction north	*[-]*	*9.00 x 10⁻⁰²*	*9.00 x 10⁻⁰²*	*9.00 x 10⁻⁰²*	*j*
Fraction of wind from direction north-east	*[-]*	*1.00 x 10⁻⁰¹*	*1.00 x 10⁻⁰¹*	*1.00 x 10⁻⁰¹*	*j*
Fraction of wind from direction south-east	*[-]*	*1.20 x 10⁻⁰¹*	*1.20 x 10⁻⁰¹*	*1.20 x 10⁻⁰¹*	*j*
Fraction of wind from direction south	*[-]*	*1.50 x 10⁻⁰¹*	*1.50 x 10⁻⁰¹*	*1.50 x 10⁻⁰¹*	*j*
Fraction of wind from direction south-west	*[-]*	*2.00 x 10⁻⁰¹*	*2.00 x 10⁻⁰¹*	*2.00 x 10⁻⁰¹*	*j*
Fraction of wind from direction west	*[-]*	*1.60 x 10⁰¹*	*1.60 x 10⁻⁰¹*	*1.60 x 10⁻⁰¹*	*j*
Fraction of wind from direction north-west	*[-]*	*1.00 x 10⁻⁰¹*	*1.00 x 10⁻⁰¹*	*1.00 x 10⁻⁰¹*	*j*
Orientation of the up- with regard to the midstream area	*[-]*	*S*	*S*	*S*	*-*
Orientation of the mid- with regard to the down-stream area	*[-]*	*SE*	*SE*	*SE*	*-*
Rain intensity	*[m.s⁻¹]*	*1.10 x 10⁰³*	*8.23 x 10⁰²*	*9.21 x 10⁰²*	*k, v, j*
Infiltration fraction in floodplain soil	*[-]*	*8.50 x 10⁻⁰¹*	*9.00 x 10⁻⁰¹*	*8.50 x 10⁻⁰¹*	*e*
Infiltration fraction in catchment soil	*[-]*	*7.50 x 10⁻⁰¹*	*8.50 x 10⁻⁰¹*	*8.50 x 10⁻⁰¹*	*e*
Fraction of rainwater as subsurface flow soil	*[-]*	*3.60 x 10⁻⁰²*	*3.60 x 10⁻⁰²*	*3.60 x 10⁻⁰²*	*-*
Fraction of rainwater as tube flow cropland soil	*[-]*	*2.50 x 10⁻⁰¹*	*2.50 x 10⁻⁰¹*	*2.50 x 10⁻⁰¹*	*e*
Fraction of rainwater as tube flow pasture soil	*[-]*	*2.50 x 10⁻⁰¹*	*2.50 x 10⁻⁰¹*	*2.50 x 10⁻⁰¹*	*e*
Fraction of rainwater exported to deep aquifers floodplain	*[-]*	*0.00 x 10⁰⁰*	*0.00 x 10⁰⁰*	*0.00 x 10⁰⁰*	*-*
Fraction of rain water exported to deep aquifers catchment	*[-]*	*1.70 x 10⁻⁰¹*	*1.70 x 10⁻⁰¹*	*1.70 x 10⁻⁰¹*	*l*

Environmental parameter	Unit	Value up-stream	Value mid-stream	Value down-stream	Reference
Fraction of soil water discharging to primary waters	[-]	5.00×10^{-01}	5.00×10^{-01}	5.00×10^{-01}	-
Fraction of soil water discharging to secondary waters	[-]	5.00×10^{-01}	5.00×10^{-01}	5.00×10^{-01}	-
Temperature	[°C]	8.20×10^{00}	9.90×10^{00}	9.70×10^{00}	k, v, j
Specific aerosol surface	[$m^2.m^{-3}$]	1.50×10^{-04}	1.50×10^{-04}	1.50×10^{-04}	b
Mass fraction organic carbon in suspended matter	[-]	2.00×10^{-01}	2.00×10^{-01}	2.00×10^{-01}	m
Fat content of fresh water fish	[-]	5.00×10^{-02}	5.00×10^{-02}	5.00×10^{-02}	b
Concentration biota in fresh water	[$mg.l^{-1}$]	1.00×10^{00}	1.00×10^{00}	1.00×10^{00}	b
Concentration suspended matter in river water	[$mg.l^{-1}$]	1.50×10^{01}	2.90×10^{01}	3.50×10^{01}	n, w, y
Concentration suspended matter in primary waters	[$mg.l^{-1}$]	5.00×10^{00}	5.00×10^{00}	5.00×10^{00}	-
Concentration suspended matter in secondary waters	[$mg.l^{-1}$]	1.50×10^{01}	2.90×10^{01}	3.50×10^{01}	n, w, y
Mass fraction organic carbon in sediment	[-]	2.00×10^{-02}	2.00×10^{-02}	2.00×10^{-02}	o
Mass fraction organic carbon in unsaturated soil	[-]	2.00×10^{-02}	2.00×10^{-02}	2.00×10^{-02}	b
Mass fraction organic carbon in saturated soil	[-]	6.00×10^{-03}	6.00×10^{-03}	6.00×10^{-03}	o
Deposition velocity of aerosol particles agricultural soil	[$m.s^{-1}$]	5.31×10^{-04}	5.31×10^{-04}	5.31×10^{-04}	p
Deposition velocity of aerosol particles natural soil	[$m.s^{-1}$]	7.30×10^{-03}	7.30×10^{-03}	7.30×10^{-03}	q
Aerosol collection efficiency	[-]	2.00×10^{05}	2.00×10^{05}	2.00×10^{05}	r
Interception of dry aerosol deposition vegetation	[-]	4.40×10^{-01}	4.40×10^{-01}	4.40×10^{-01}	s
Interception of wet aerosol deposition vegetation	[-]	1.40×10^{-01}	1.40×10^{-01}	1.40×10^{-01}	t
Growth rate natural vegetation	[s^{-1}]	2.88×10^{-08}	2.88×10^{-08}	2.88×10^{-08}	i
Growth rate agricultural vegetation	[s^{-1}]	1.27×10^{-07}	1.27×10^{-07}	1.27×10^{-07}	i
Harvesting efficiency natural vegetation	[-]	0.00×10^{00}	0.00×10^{00}	0.00×10^{00}	b
Harvesting efficiency agricultural vegetation	[-]	5.90×10^{-01}	5.90×10^{-01}	5.90×10^{-01}	b
Water absorption rate natural vegetation	[$m.s^{-1}$]	8.40×10^{-09}	8.40×10^{-09}	8.40×10^{-09}	i
Water absorption rate agricultural vegetation	[$m.s^{-1}$]	9.32×10^{-09}	9.32×10^{-09}	9.32×10^{-09}	i
Settling velocity of suspended particles	[$m.s^{-1}$]	2.89×10^{-05}	2.89×10^{-05}	2.89×10^{-05}	b
Autochthonous production of suspended matter in water	[$g.m^{-2}.y^{-1}$]	1.00×10^{01}	1.00×10^{01}	1.00×10^{01}	b
Net sediment accumulation rate in water	[$m.s^{-1}$]	2.36×10^{-11}	3.17×10^{-11}	4.44×10^{-11}	u, x, y
Erosion in floodplain zone	[$m.s^{-1}$]	6.00×10^{-02}	1.00×10^{-02}	1.00×10^{-04}	n
Erosion in catchment zone	[$m.s^{-1}$]	9.00×10^{-02}	3.00×10^{-02}	1.00×10^{-03}	n

Environmental parameter	*Unit*	*Value up-stream*	*Value mid-stream*	*Value down-stream*	*Reference*
Escape of air to the stratosphere	$[s^{-1}]$	3.66×10^{-10}	3.66×10^{-10}	3.66×10^{-10}	*b*
Regional OH-radical concentration	$[cm^{-3}]$	5.00×10^{05}	5.00×10^{05}	5.00×10^{05}	*b*
Mechanical reworking depth agricultural soils	[m]	2.00×10^{-01}	2.00×10^{-01}	2.00×10^{-01}	*b*
Tube drainage depth	[m]	1.00×10^{00}	1.00×10^{00}	1.00×10^{00}	*e*
Depth of transpiration flow pasture vegetation	[m]	2.00×10^{-01}	2.00×10^{-01}	2.00×10^{-01}	*z*
Depth of transpiration flow cropland vegetation	[m]	2.00×10^{-01}	2.00×10^{-01}	2.00×10^{-01}	*z*
Depth of transpiration flow natural vegetation	[m]	8.00×10^{-01}	8.00×10^{-01}	8.00×10^{-01}	*z*
Population density	$[km^{-2}]$	1.99×10^{02}	2.34×10^{02}	3.89×10^{02}	*a*
Emission dose	$[kg.\ km^{-2}]$	3.17×10^{00}	2.60×10^{00}	8.27×10^{00}	*aa*

References: a = Nationmaster (2005). b = Den Hollander and Van de Meent (2004). c= McKone (1993). d = CLM (2004). e = Tiktak et al. (2002). f = Paterson and Mackay (1994). g = Scurlock et al. (2001). h = Zeng et al. (2000). i = Severinsen and Jager (1998). j = KNMI (2004). k = MeteoSchweiz (2004). l = De Wit (1999). m = Zhang et al. (2003). n = Asselman (1997). o = McKone et al. (2001). p = McLachlan et al. (2002). q = Horstmann and McLachlan (1998). r = Mackay (1991). s = Chamberlain (1967). t = Scheringer et al. (2000). u = Schwarzenbach et al. (1993). v = DWD (2004). w = Meybeck et al. (2003). x = Trapp (1996). y = Hofstee and Leenaers (2002). z = Jackson (1996). aa = FAO (2001).

Table 4: Environmental input parameters for the BasinBox model in the case study for the river Rhine catchment.

half-lives in air and water (and soil). Since the calculations were performed for five values of the degradation half-life in water and five values of the degradation half-life in air, for each combination of emission scenario and compartment 25 plots can be made. It appeared that the degradation rate of compounds in air hardly influenced the concentration ratios in our calculations, so plots were created for only one value of the degradation half-life in air. We used the median of the modeled values of the half-life in air (168 h). The plots provide a clear overview of chemical property combinations causing large spatial variation in the predictions of BasinBox.

Results and discussion

Table 5 shows for all combinations of emission scenario and compartment type the percentage of hypothetical chemicals for which the predicted concentrations of BasinBox in the upstream and downstream areas differ more than a factor of 10 and 100, respectively. In more than 95% of all cases, downstream concentrations are higher than upstream concentrations, implying that there is a clear trend of increasing chemical concentrations in downstream direction of the Rhine

Floodplain compartments												
Ratio >10	*Emission:*	*Air*	*River*	*River sediment*	*Pasture soil*	*Pasture vegetation*	*Cropland Soil*	*Cropland vegetation*	*Natural soil*	*Natural vegetation*	*Saturated soil*	
	Air	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	
	River	*0.00*	*0.00*	*0.00*	*16.50*	*0.00*	*16.20*	*0.00*	*8.50*	*0.00*	*0.50*	
	Soil	*21.60*	*0.00*	*0.00*	*19.50*	*20.40*	*0.00*	*18.20*	*19.50*	*20.10*	*7.20*	
Catchment compartments												
Ratio >10	*Emission:*	*Pasture soil*	*Pasture vegetation*	*Cropland soil*	*Cropland vegetation*	*Natural soil*	*Natural vegetation*	*Saturated soil*	*Primary waters*	*Primary water sediment*	*Secondary waters*	*Secondary water sediment*
	Air	*0.00*	*0.00*	*0.00*	*0.00*	*5.20*	*0.00*	*0.00*	*0.60*	*2.70*	*0.00*	*0.00*
	River	*0.00*	*0.00*	*0.00*	*0.00*	*10.60*	*0.00*	*0.00*	*0.20*	*1.40*	*0.00*	*0.00*
	Soil	*17.60*	*28.50*	*0.00*	*15.10*	*62.00*	*13.40*	*0.50*	*6.00*	*7.60*	*0.00*	*0.00*
Floodplain compartments												
Ratio >100	*Emission:*	*Air*	*River*	*River sediment*	*Pasture soil*	*Pasture vegetation*	*Cropland soil*	*Cropland vegetation*	*Natural soil*	*Natural vegetation*	*Saturated soil*	
	Air	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	
	River	*0.00*	*0.00*	*0.00*	*1.60*	*0.00*	*1.90*	*0.00*	*0.00*	*0.00*	*0.00*	
	Soil	*2.20*	*0.00*	*0.00*	*1.60*	*2.10*	*0.00*	*2.10*	*1.60*	*2.10*	*0.00*	
Catchment compartments												
Ratio >100	*Emission:*	*Pasture soil*	*Pasture vegetation*	*Cropland soil*	*Cropland vegetation*	*Natural soil*	*Natural vegetation*	*Saturated soil*	*Primary waters*	*Primary water sediment*	*Secondary waters*	*Secondary water sediment*
	Air	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*
	River	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*
	Soil	*1.60*	*2.60*	*0.00*	*1.90*	*1.10*	*1.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*

Table 5: Percentage of all hypothetical chemicals that show a concentration ratio larger than 10 and 100, per compartment type, per emission scenario.

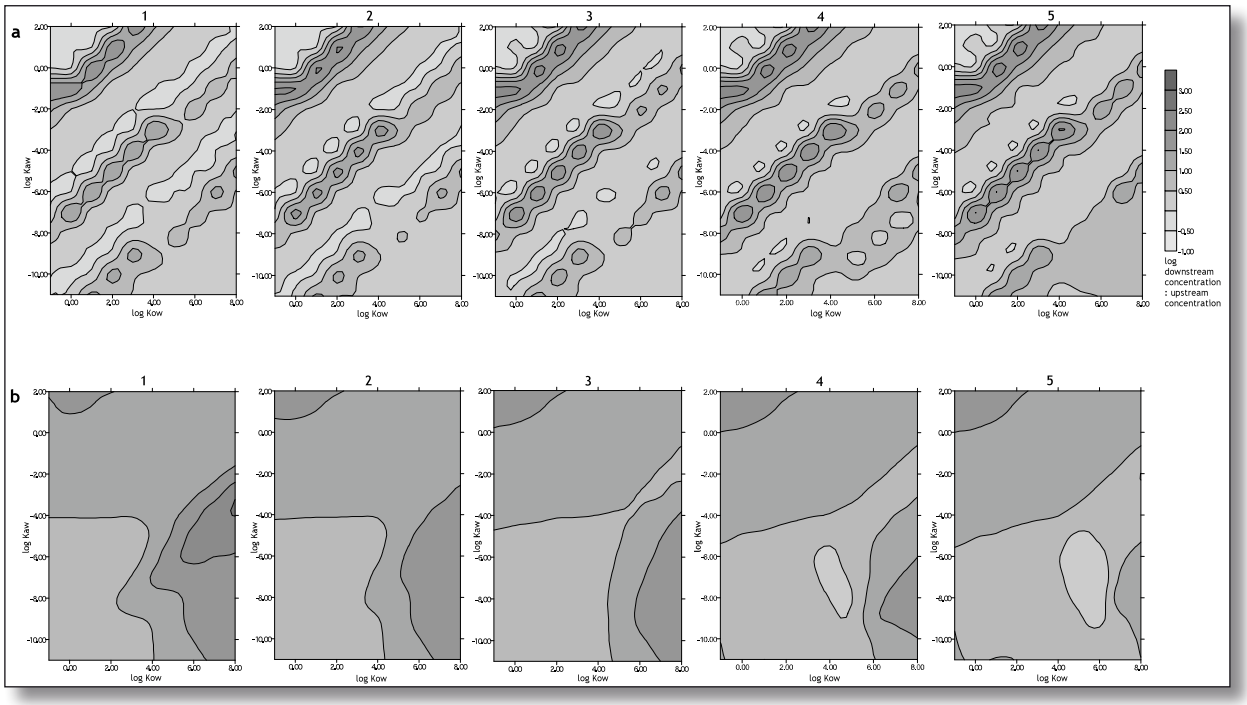
basin area. This is mainly caused by differences in emissions between the upstream and downstream area. Since the upstream area of the Rhine basin is less densely populated and contains less agricultural soils, emissions to air, river water as well as cropland soils are lower than in the downstream area. Furthermore, water based transport of chemicals, which occurs in downward direction of the river basin, causes variation in chemical concentrations between the upstream and downstream areas. For the river and floodplain compartments, the influence of downward transport can account for up to 60% of the concentration variance between the upstream and downstream areas, particularly when emissions occur to water. For the catchment compartments this downward chemical transport is only of minor influence.

For 13 combinations of emission scenario and compartment type concentration ratios >100 appeared. For all these scenarios, series of chemical space plots were created, consisting of five separate plots for all five modeled values of the degradation half-life in water (and soil). Two series of chemical space plots are given in Figure 15, while the full set of plots is given in Appendix B1.

River water emission scenario

In case of emissions towards river water, relatively large spatial differences (ratio >100) are found for about 60 chemical property combinations in cropland soils and pasture soils in the floodplain. Figure 15a shows the chemical space plots for the cropland soil compartment in the floodplain. The main transport routes responsible for the concentration differences are (1) downward transport of chemicals by river water and (2) temporal inundation of downstream floodplain soils and subsequent sedimentation of chemicals onto these soils. Beside that, variations in emission densities between the upstream and downstream areas account for concentration differences. For the natural soil compartments in the floodplain, concentration ratios are somewhat lower, but still larger than 10 for 8.5% of the chemicals. As a result of high concentration ratios in the floodplain soils, also the saturated soil zone in the floodplain shows concentration ratios >10 for some compounds.

In floodplain pasture and cropland soils, chemical property combinations for which the concentration ratio is larger than 100 range between a log K_{aw} of 0 to 2 with a log K_{ow} of 8. These chemicals have a high volatilisation potential from water to air on the one hand, and tend to bind to organic material on the other hand. So, when sedimentation in the floodplain occurs, a large part of these chemicals will settle down to the floodplain soils. Only compounds with a relatively high half-life in water (8760 to 87,600 h) and soil (17,520 to 175,200 h) will show relatively large concentration differences between the upstream and the downstream areas. The degradation half-life of chemicals in air does not largely influence the fate of chemicals. Not many chemicals exist for which the above-mentioned property combinations apply, but octachloro-2-pinene (cas# 25267-15-6; pesticide; PAN, 2005) and 1-iodohexadecane (cas# 544-77-4; pesticide; PAN, 2005) are known compounds in this range. For cropland soils in floodplains, the same applies as for pasture soils, but the range of chemicals for which large concentration ratios occur is somewhat broader.



Chemicals with a log K_{aw} of –7, a log K_{ow} of 8 and a water degradation half-life of 8760 h, as well as chemicals with a log K_{aw} of –5, a log K_{ow} of 7 and a water degradation half-life of 24 h show concentration ratios >100. Examples of chemicals that have the above-mentioned chemical property combinations are monomethyl ester (cas# 6983-79-5; pesticide; PAN, 2005) and isodecyl-diphenyl phosphate (cas# 29761-21-5; plasticizer/flame retardant; Chemicalland21, 2005), respectively.

Figure 15: Chemical space plots for cropland soils in the floodplain by emission to river water and a degradation half-life in air of 168 h (15a), and for natural soils in the catchment by emission to croplands and a degradation half-life in air of 168 h (15b). The numbers 1 to 5 in Figure 15a and 15b represent the different degradation half-lives in water: 1 = 24 h, 2 = 168 h, 3 = 1000 h, 4 = 8760 h, 5 = 87600 h. Chemical property combinations represented in the upper left and lower right triangles of the plots are not likely to occur in reality and are not included in the dataset of hypothetical chemicals used in this study.

Cropland soil emission scenario

For the emission scenario to cropland soils, eleven compartment types show a concentration ratio be-

tween the downstream and upstream areas larger than 100 for a number of hypothetical chemicals. This is the case for the air compartment, all soil and vegetation compartments in the floodplain zone, pasture soils and natural soils in the catchment zone and pasture, cropland and natural vegetation in the catchment zone. The large ratios are mainly caused by differences in emission densities, followed by differences in the volatilization of chemicals from soil and vegetation to the air. In the saturated soil and in primary waters, concentration differences larger than a factor of 10 occur. These differences are a direct consequence of concentration differences in the soil compartments, which results in different chemical amounts leaching to the saturated soil zone and draining to the surface water compartments.

The series of chemical space plots for the natural soil compartment in the catchment for the soil emission scenario is shown in Figure 15b, but this situation applies approximately for all compartments with emissions to soils and concentration ratios >100. Chemicals with a log K_{aw} ranging from -6 to -3 and a log K_{ow} from 5 or 6 to 8 show the largest concentration ratios. These compounds tend to bind to organic material on the one hand and are not very volatile on the other hand. Large concentration ratios are only found for chemicals with degradation half-lives in water of 24 or 168 h. This is caused by differences in the soil penetration depth of the chemicals, which is low for compounds with low degradation half-lives in water and soil. As a result, the process of volatilization becomes relatively important for those compounds, so in case of emissions taking place to the cropland soil compartments, the differences in emission densities between the upstream and downstream areas are being strengthened by this volatilization flow. Therefore, large concentration differences arise in the upstream and downstream areas. In cropland soils theirselves, the concentration ratio is not so large, since for those compartments the emission process is much more important than the volatilization flow. Consequently, the concentration ratio in the cropland soil compartments equals more or less the soil emission ratio. As is the case by emissions to river water, the degradation half-life of chemicals in air does hardly influence their fate. Examples of real chemicals having the property combinations that result in large concentration differences between the upstream and downstream areas are tributyltin adipate (cas# 7437-35-6; pesticide; PAN, 2005), oleic acid (cas# 112-80-1; high production volume chemical, used in consumer products, building materials and pesticides; Scorecard, 2005), dicyclohexyl phtalate (cas# 84-61-7; high production volume chemical, used as plasticizer; Scorecard, 2005), and tetradecanol (cas# 112-72-1; high production volume chemical, used in consumer products, building materials and pesticides; Scorecard, 2005).

Air emission scenario

In case of emissions occurring towards the air compartments, none of the compartment types shows a concentration ratio between the upstream and downstream areas larger than 100, and only a few compartment types show a ratio larger than 10. Due to rapid mixing of chemicals in the atmosphere and because air-based chemical transport takes place both in upstream and in downstream directions, the concentra-

tion differences between the downstream area and the upstream area remain relatively low.

Uncertainty

From these calculations it becomes clear, that for certain types of chemicals large concentration differences can exist within one river basin. One remark should be made on the model results for the compounds with low degradation half-lives in air, water and soil and with a high K_{ow} (half-life in water of 24 h, log K_{ow} from 7-8). Although these compounds have a low soil penetration depth in reality, predicted soil penetration depths are even considerably lower. The algorithm of the soil penetration depth in BasinBox was primarily designed for compounds with less extreme property combinations, and it is not possible to extrapolate it directly to all chemicals. Therefore, the concept of the soil penetration depth in BasinBox does not apply very well on extreme hydrophobic and rapidly degrading compounds. Since the soil penetration depth largely influences the concentration ratios, especially when emissions take place to the soil, for these compounds the model results are not very reliable. However, for the other compounds the model relations do apply and compounds showing large concentration ratios still exist.

The relevance of the BasinBox model not only depends on relative differences that are found between the upstream, midstream and downstream areas of a river basin, but also on the absolute concentration differences. When concentration differences are large, but absolute chemical concentrations are very low, knowledge about the concentration differences is not very relevant. Since the example calculations were based on relative emissions, the model predicts only relative concentrations. To get an idea about absolute concentrations anyhow, we compared the relative concentrations in cropland soils and in natural soils after emission of chemicals to cropland soils. We assumed that if natural soil concentrations are less than six orders of magnitude lower than cropland soil concentrations (after cropland soil emission), these concentrations might be of serious concern. This appeared to be the case for 89% of the hypothetical chemicals, and for 76% of the chemicals that show concentration ratios >100 between downstream and upstream areas. For 10% of all chemicals the natural soil concentrations are even less than three orders of magnitude lower than cropland concentrations. These numbers indicate that for a large number of chemicals seriously high concentrations can be found, in any case in natural soils. For these chemicals also knowledge about concentration variances will be relevant.

Although it is quite difficult to validate this type of generic models with such a large amount of compartments, a validation study has to be carried out to judge whether the spatial variation in predicted concentrations in BasinBox agrees with actual concentration differences throughout a river basin. In a next step in research we will perform a validation study for the BasinBox model using real chemical data in different river catchments, based on real emission scenarios.

Conclusion

BasinBox is a new generic multimedia fate model that predicts environmental concentrations of chemicals

in large river basins. It distinguishes an upstream, midstream, and downstream area with different environmental characteristics. Water transport is modeled in a downward direction, and floodplain inundations are taken into account. It appears that BasinBox predicts significant concentration differences between upstream and downstream areas of the river Rhine basin for different types of chemicals and different emission scenarios. There is a clear trend of increasing chemical concentrations in the downstream direction of the river basin. This case study shows that taking into account spatial variability between upstream, midstream and downstream areas of large river basins can be important in the predictions of environmental concentrations by multimedia fate models.

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5 Spatial variance in multimedia mass balance models: comparison of LOTOS-EUROS and SimpleBox for PCB-153

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Abstract

The aim of this study was to determine whether nested generic box models can be used to predict spatial variance. An inter-comparison study was performed for the nested box model SimpleBox, and the spatially resolved model LOTOS-EUROS, using PCB-153 emissions in Europe as an example. We compared the two models concerning 1) average environmental concentrations, 2) spatial concentration variances, 3) spatial concentration patterns (maps), and 4) agreement with measured concentrations for the air and soil compartments. In SimpleBox, the spatial concentration variances and patterns were calculated subsequently for each separate grid cell surrounded by a regional and a continental shell with homogeneous, averaged circumstances. Average European PCB-153 concentrations calculated by LOTOS-EUROS and SimpleBox for the period 1981-2000 agree well for the air and soil compartments. Moreover, the predicted concentrations of both models are in line with the measured PCB-153 concentrations in Europe during that period. For PCB-153, the prediction of spatial concentration variances with the nested multimedia fate model SimpleBox performs adequately in most cases, except for the lower concentration boundary in the air compartment. It is concluded that SimpleBox can be used to predict the spatial maximum and average concentrations of PCB-153 in the air and soil compartments. The proposed method has to be tested systematically for different types of compounds, emission scenarios, environmental compartments and spatial scales in order to allow conclusions about the general applicability of the method.

Introduction

Over the past decades, the use of multimedia mass balance models to predict the environmental fate of Persistent Organic Pollutants (POPs) has strongly increased. Multimedia mass balance models were originally developed for the screening and evaluation of the environmental fate of toxic substances and therefore make rather rough estimations of environmental concentrations (Cowan et al., 1995; Mackay, 2001). These models have proven to be very useful tools in chemical risk management, due to their relatively low complexity and multimedia character. In the European Union, the EUSES model (Vermeire et al., 1997; 2005) is currently being used as a risk policy instrument, while in the USA, CalTOX (McKone, 1993) and the Total Risk Integrated Methodology (TRIM.FaTE; US-EPA, 2002) are typically applied for this purpose.

Though, throughout the years, also more refined multimedia fate models were developed, which can be distinguished from each other based on compartmentation or process descriptions (Mackay et al., 1997; Wania and Mackay, 1999). These models enable the user to make more accurate predictions about environmental concentrations under specific conditions. Besides, a new trend appears towards the development of spatially resolved multimedia fate models. In 1996, Wania tentatively screened the possibilities for introducing GIS in multimedia fate models (Wania, 1996). More advanced vector- and grid-based multimedia fate models followed, such as IMPACT-2002 (Pennington et al., 2005), BETR-Europe (Prevedouros et al., 2004), and BETR-Global (MacLeod et al., 2005). Nowadays even very detailed models exist, up to a resolution of a few square kilometers (G-Ciems; Suzuki et al., 2005).

Both spatial and non-spatial generic multimedia mass balance models can be applied for the prediction of POP environmental fate, depending on the specific purpose of the modeling study (Cahill and Mackay, 2003). With multimedia box models, for example, it is relatively easy to treat large groups of compounds or scenarios in one study. The advantage of the more detailed types of models is that they do not only predict average concentrations, but also minimum and maximum concentrations, their abundance, and concentration ranges. Moreover, the locations are estimated where high and low chemical concentrations can be expected. However, for many risk assessment studies, insight in average concentrations as well as peak concentrations suffices (Klepper and Den Hollander, 1999). In those situations, it is sufficient to know the average and the spatial variance in environmental concentrations without knowing exactly where those concentrations occur. The question is whether non-spatial nested box models can be used for that purpose. Since calculations with box models are generally more transparent and user-friendly, their use may be preferable in those cases. Although several comparison studies have been performed between spatial and non-spatial models (e.g. Margni et al., 2004, Shatalov et al., 2004; 2006, Pennington et al., 2005), spatial concentration variances predicted by spatial models and non-spatial nested box models have hardly been compared.

The aim of this study was to explore the potential of nested box models to predict spatial concentra-

tion variances in the air and soil compartments. We performed an inter-comparison study for the nested box model SimpleBox, and the spatially resolved, dynamic atmospheric transport model LOTOS-EUROS, using PCB-153 emissions in Europe as an example. LOTOS-EUROS is a recently developed model, originated from the existing models LOTOS and EUROS (Schaap et al., 2005). We compared its results with those of SimpleBox, which is a commonly used generic multimedia mass balance model that has been validated for several substances and applications (Den Hollander et al., 2004). PCB-153 was chosen as a testing compound, since European emission data and measured concentration data in air and soil were available for the period 1981-2000. We compared the two models concerning 1) average environmental concentrations, 2) spatial concentration variances, 3) spatial concentration patterns (maps), and 4) agreement with measured concentrations.

Material and methods

Models

LOTOS-EUROS

The LOTOS and the EUROS models were developed independently by respectively the Netherlands Organization for Applied Scientific Research (TNO; Builtjes, 1992; Schaap et al., 2004) and the National Institute of Public Health and the Environment (RIVM; De Leeuw and Van Reineck Leyssius, 1990; Van Loon, 1994, 1995; Matthijsen et al., 2002) to calculate the dispersion and chemical transformation of air pollutants in the lower troposphere of Europe. EUROS had a module to simulate the fate of persistent organic pollutants (POPs), which included soil and surface water compartments (Jacobs and Van Pul, 1996). In 2005, LOTOS and EUROS were merged into the present model LOTOS-EUROS version 1.0 (Schaap et al., 2005a; 2005b, Schaap et al., 2008). In this new model, the POP-module of EUROS was implemented, which was used for this study.

LOTOS-EUROS is a dynamic model, calculating environmental concentrations and fluxes every three hours. The calculation domain of LOTOS-EUROS is defined by the boundaries 35 °N and 70 °N, and 10 °W and 40 °E. The standard grid resolution is 0.50 °longitude x 0.25 °latitude, approximately 25 x 25 km, which means that LOTOS-EUROS counts 14,000 grid cells.

The model extends in vertical direction 3500 m above sea level, divided into four atmospheric layers: an optional surface layer of 25 m, a dynamic mixing layer and two reservoir layers. Beside the air compartments, the POPs-version of the model distinguishes sea water, fresh water and soil compartments. The modeled soil has a thickness of 15 cm, divided into five layers: a surface layer of 0.5 cm, followed by layers of 0.5, 1.0, 2.0 and 11.0 cm. In all soil layers, the volume fractions of solids, water and air were set respectively to 0.5, 0.27 and 0.23. Two land-use types are distinguished: agricultural and non-agricultural. The fresh water and the sea water compartments are both represented as homogeneous boxes within a grid cell, the fresh water compartment having a depth of 25 m and the seawater compartment a depth of 200 m.

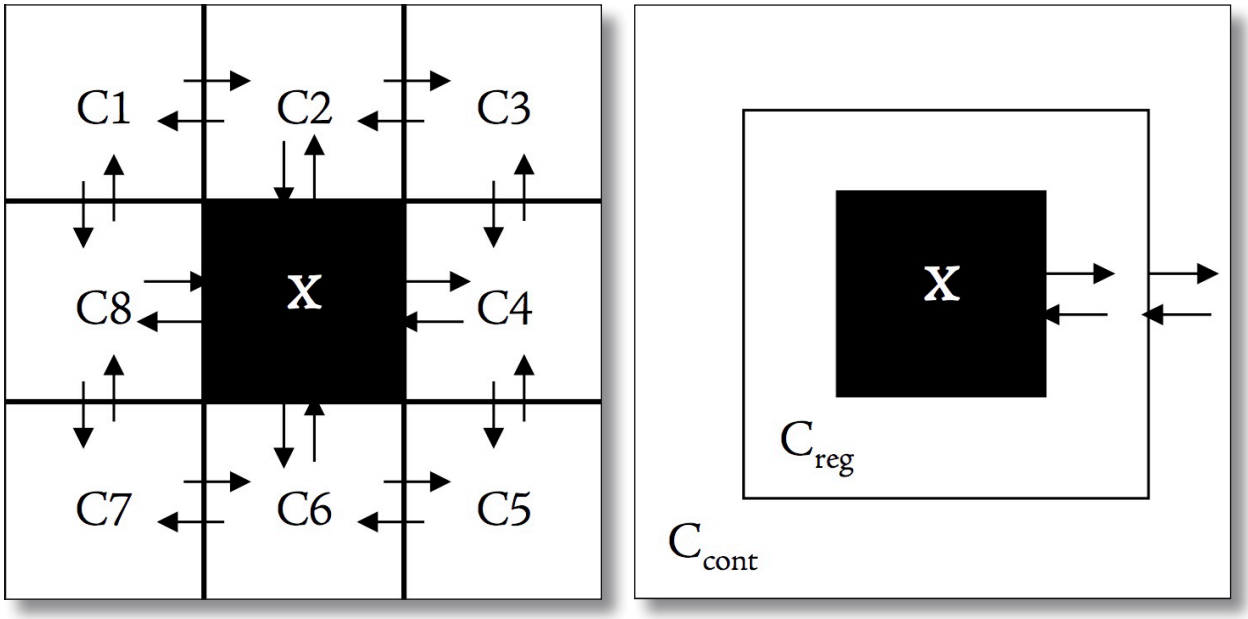


Figure 16: Schematic representation of the two ways of calculating environmental concentrations in the selected grid cell X. 16a (left): The situation in LOTOS-EUROS. C1-8 represents the concentration in grid cell 1 to 8. 16b (right): The situation in SimpleBox. C_{reg} stands for the average concentration on the regional scale, C_{cont} represents the average concentration in the whole calculation domain.

SimpleBox 3.0

SimpleBox is a nested level III and level IV "Mackay type" multimedia fate model consisting of ten environmental compartments on local, regional, continental and global scales (Brandes et al., 1996; Den Hollander et al., 2004). The regional and continental scales distinguish an air compartment (atmospheric mixing layer), a sea water compartment with a sediment compartment, a fresh water compartment with a sediment compartment, and three types of soil compartments (natural, agricultural, other soil) with corresponding vegetation compartments (natural and agricultural vegetation). The local scale is designed in the same way as the regional scale, except that on this scale the sea water compartment is missing. On the global scales, all soil types are combined in one box and fresh water and vegetation compartments are lacking. Chemical transport between the different scales occurs by air and water transport. SimpleBox is a generic model, in which the default settings of the local, regional and continental scales of the model are set to match the European Union procedures for the evaluation of substances (Brandes et al., 1996).

Model comparison

The two ways of calculating environmental concentrations in all grid cells by both models are represented schematically in Figure 16. In Figure 16a, the situation in LOTOS-EUROS is given, with a grid of cells with different environmental characteristics and concentrations. Chemical exchange between the different grid cells occurs by air and sea water flows. In a computational intensive calculation, concentrations in cells are calculated simultaneously. Figure 16b shows the situation in SimpleBox, where the local scale area (representing one specific grid cell of the LOTOS-EUROS calculation domain) is surrounded by a regional and a continental shell (the total calculation domain), both with homogeneous, averaged circumstances. The model is repeatedly run for the separate grid cells, so the environmental concentrations are calculated for each cell consecutively in SimpleBox.

For the comparison study, the model dimensions of LOTOS-EUROS 1.0 and the level IV-type version of SimpleBox 3.0, and their environmental input parameters were homogenized, while the model specific chemical transport algorithms were maintained. For this purpose, the local scale of SimpleBox was set equal to the approximate size of one grid cell in LOTOS-EUROS (25 x 25 km), the regional scale maintained its size of 200 x 200 km, while the continental scale was set to represent the whole European calculation domain. The vegetation compartments of SimpleBox were turned off and the depth of all fresh water compartments was set to 25 meters, while the sea water depth on the regional scale was set to 200 meters. The volume fractions of solids, water and air in the soil compartments were assumed to be 0.5, 0.27 and 0.23 respectively. The depth of all soil compartments was set to 15 cm. The 'agricultural soil' land-use fraction of each cell of LOTOS-EUROS was applied in SimpleBox, while the remaining soil fraction was divided over 'natural soils' and 'other soils' with a ratio of 3:1 (as is default in SimpleBox 3.0; Den Hollander et al., 2004).

The spatially and temporally variable input data atmospheric temperature, soil temperature, rain fall, snow fall, air humidity, horizontal and vertical wind speed, and atmospheric mixing layer height as well as the emissions were entered to each grid cell for each time step in LOTOS-EUROS. Soil organic carbon contents and land use fractions were considered spatially variable, but constant in time during the calculation period. The grid cell specific input data are summarized in Table 6. Environmental concentrations were calculated with time steps of three hours. Consecutively, for each of the grid cells, the SimpleBox model was run with the same location specific input, except soil temperature, vertical wind velocity and air humidity, since those parameters are not taken into account in the model algorithms (see Table 6). On the regional scale, the parameter values of the 63 grid cells surrounding the local scale cell were averaged and emissions were summed up to cover an area of 200 x 200 km. On the continental scale, average European values were maintained. Like LOTOS-EUROS, the SimpleBox model was run for the period 1981-2000, but with time steps of one month.

Parameter	*LOTOS-EUROS*	*SimpleBox*
Spatially and temporally variable parameters:		
Mixing height of lower atmospheric layer	✓	✓
Atmospheric temperature	✓	✓
Air humidity	✓	–
Precipitation intensity	–	✓
Rain fall intensity	✓	–
*Snow fall intensity**	✓	–
Horizontal wind velocity at 10 m	✓	✓
Vertical wind velocity at 10 m	✓	–
Soil temperature	✓	–
Emissions	✓	✓
Spatially variable parameters:		
Area fraction sea water	✓	✓
Area fraction fresh water	✓	✓
Area fraction agricultural soil	✓	✓
Area fraction natural soil	–	✓
Area fraction other soil	–	✓
Area fraction non-agricultural soil	✓	–
Soil organic carbon content	✓	✓

** A conversion was made from rainfall and snowfall data in LOTOS-EUROS to one value for precipitation in SimpleBox. For this, 10 mm of snowfall was put on the same level as 1 mm of rain (CSAC, 2006).*

Table 6: Grid cell specific input parameters for LOTOS-EUROS and SimpleBox.

The models were run for the emission scenario of PCB-153 in Europe in the period 1981-2000. PCB-153 is mainly being used as an insulation liquid, as a softener in plastics and for roofing (Enius, 2006). This compound was chosen, since emission and validation data were available, and since PCB-153 has a 'multimedia character', which means that after emission, it is being distributed among different environmental compartments. Yearly-averaged emission data on a 1 x 1 degree scale were derived from Breivik et al. (2002), converted to grid-format as described by Shatalov et al. (2006) for use in a large POP-model inter-comparison study being performed by MSC-E (Shatalov et al., 2004; 2006). The physical-chemical input data for PCB-153

Parameter	*Value*	*Unit*	*Reference*
Molecular weight	$3.61*10^{+2}$	$g.mol^{-1}$	*Mackay et al., 1992*
Vapor pressure at 25°C	$8.82*10^{-5}$	*Pa*	*Li et al, 2003*
Water solubility at 25°C	$6.50*10^{-3}$	$mg.l^{-1}$	*Li et al, 2003*
K_{ow}	$1.45*10^{+7}$	-	*Li et al, 2003*
Gas/water partition coefficient at 25°C	$2.09*10^{-3}$	-	*Li et al, 2003*
Solids/water partition coefficient at 25°C	$2.96*10^{+5}$	-	*Li et al, 2003*
Enthalpy of vaporization	$8.77*10^{+1}$	$kJ.mol^{-1}$	*Li et al, 2003*
Enthalpy of dissolution	$2.50*10^{+1}$	$kJ.mol^{-1}$	*Li et al, 2003*
Gas phase degradation rate constant at 25°C	$3.50*10^{-8}$	s^{-1}	*Mackay et al., 1992*
Dissolved phase degradation rate constant at 25°C	$3.50*10^{-9}$	s^{-1}	*Mackay et al., 1992*
Bulk degradation rate constant sediment at 25°C	$3.50*10^{-9}$	s^{-1}	*Mackay et al., 1992*
Bulk degradation rate constant soil at 25°C	$3.50*10^{-9}$	s^{-1}	*Mackay et al., 1992*

Table 7: Physical-chemical input data for PCB-153.

are given in Table 7. In SimpleBox, the emissions per grid cell were entered on the local scale of the model. On the regional scale, the emissions were summed up to cover an area of 200 x 200 km. The amount of emissions on the continental scale was defined as the total European emission minus the emission towards the considered grid cell (local scale) and the emissions towards the regional scale. Initial concentrations in both models were set to zero.

Average concentrations, spatial concentration variances, and spatial concentration patterns (maps) of PCB-153 were compared for the air and soil compartments. The spatial concentration variance is defined as the quotient between the 95th and the 5th concentration percentile of the 14,000 cell-specific concentration values. In LOTOS-EUROS, the concentrations of PCB-153 in the five soil layers were averaged by summing up the product of the concentrations and the thicknesses of the layers, and dividing it by the total soil thickness. The same was done for the PCB 153-concentrations in the two lower air layers, in order to make the results comparable to those of SimpleBox. The predicted concentration ranges were compared to measured concentrations of PCB-153 in Europe during the calculation period (see Appendix C1 for a list of measured concentrations). Maps with spatial concentration patterns were created using GRADS-software (IGES, 2006). The spatial concentration patterns of both models were compared for December 1985, which is after 5 years of calculation, in the period of maximum emission intensity.

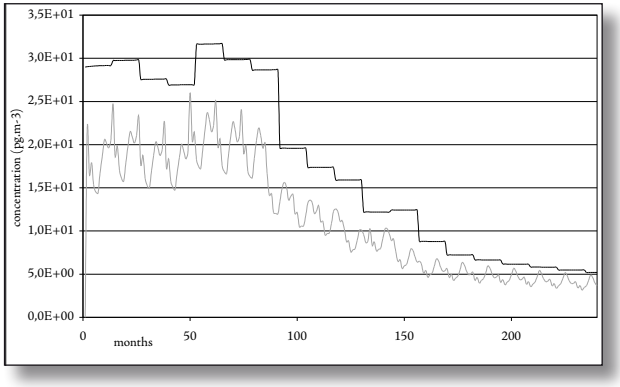


Figure 17a: Predicted average concentrations of PCB-153 in Europe in the period 1981-2000 for SimpleBox (black line) and LOTOS-EUROS (grey line). 17a (left): Air compartment.

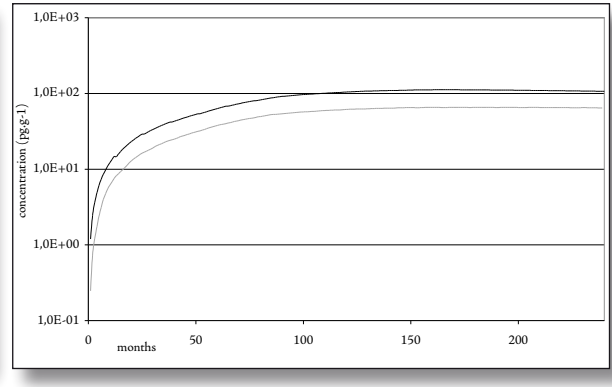


Figure 17b: Predicted average concentrations of PCB-153 in Europe in the period 1981-2000 for SimpleBox (black line) and LOTOS-EUROS (grey line). 17b (right): Soil compartment.

Results

Graphs of the predicted average concentrations of PCB-153 in Europe in the period 1981-2000 are given in Figure 17, both for SimpleBox and LOTOS-EUROS. Figure 17 shows concentrations in the air compartment and in the soil compartment, respectively. Average air concentrations in LOTOS-EUROS range from 3.2 pg.m^{-3} at the end of the calculation period to 26 pg.m^{-3} in 1986. Concentrations predicted by SimpleBox are equal to two times higher during the whole calculation period. The average air concentration over time in both SimpleBox and LOTOS-EUROS follows the emission pattern of PCB-153 in Europe over the 1981-2000 period. The average soil concentrations predicted by both models increase from 1981 to 1988 and then slightly decrease until 2000. Average concentrations are predicted to be 1.5 to three times higher in SimpleBox than in LOTOS-EUROS.

Graphs with the 5th and 95th percentile of the predicted concentrations, representing the spatial concentration variances of PCB-153 in Europe over the period 1981-2000, are shown in Figure 18. Figure 18a shows the values for the air compartments, and Figure 3b those for the soil compartments. In both models, the 5th and 95th percentile values follow the temporal pattern of the average values. For the air compartment, the upper values of LOTOS-EUROS and SimpleBox are comparable, varying from 150 to 200 pg.m^{-3}, while the lower values of SimpleBox are on average 13 times higher than those of LOTOS-EUROS. In LOTOS-EUROS, the lower concentrations range from 0.1 to 1.2 pg.m^{-3}, and in SimpleBox from 8 to 12 pg.m^{-3}. During the calculation period, the spatial concentra-

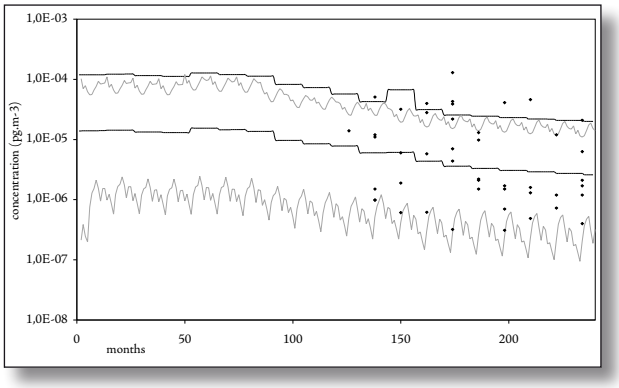


Figure 18a: Predicted spatial concentration variances of PCB-153 in Europe in the period 1981-2000 for SimpleBox (black lines) and LOTOS-EUROS (grey lines). 18a (left): the 5th- and the 95th-percentiles of the air concentrations. The black dots represent measured concentrations of PCB-153 in Europe during the calculation period.

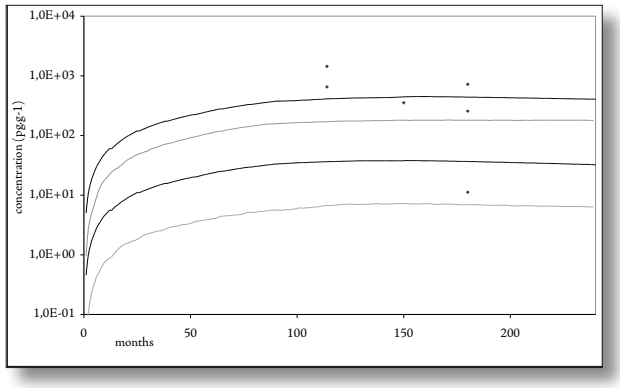
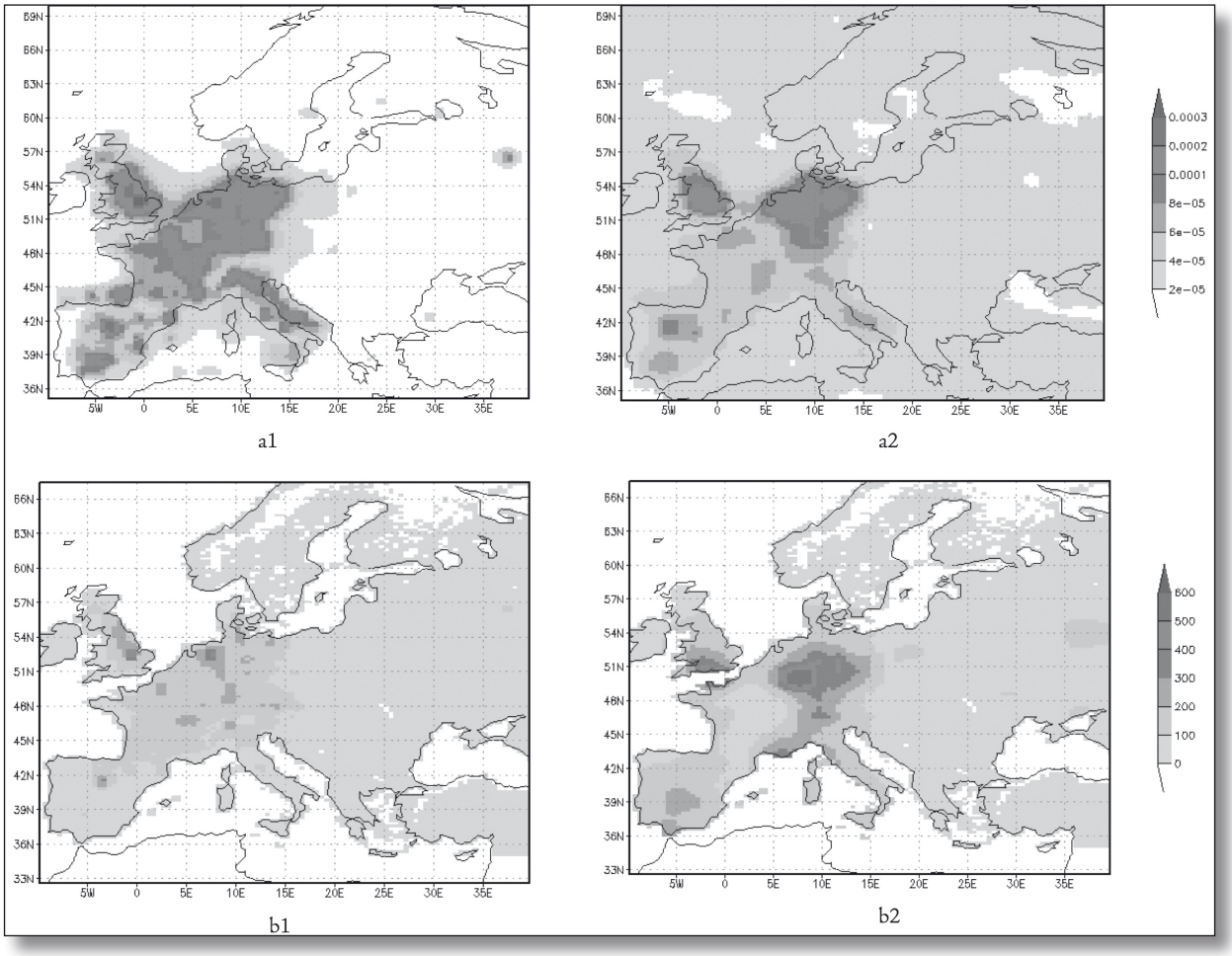


Figure 18b: Predicted spatial concentration variances of PCB-153 in Europe in the period 1981-2000 for SimpleBox (black lines) and LOTOS-EUROS (grey lines). 18b (right): The 5th- and the 95th-percentiles of the soil concentrations. The black dots represent measured concentrations of PCB-153 in Europe during the calculation period.

tion variance in LOTOS-EUROS is at maximum 480, and in SimpleBox 11. The average spatial concentration variances are 70 and 8 respectively. For the soil compartment, the spatial concentration variances of both LOTOS-EUROS and SimpleBox are in the same order of magnitude. During the calculation period, the variance in SimpleBox is at maximum 13, and the maximum variance in LOTOS-EUROS is 28. Both the 5th and the 95th percentile values are lower in LOTOS-EUROS, the lower values up to a factor of six, and the upper values up to a factor of three. In order to validate the concentration ranges predicted by SimpleBox and EUROS-LOTOS, measured concentration values of PCB-153 were also plotted in Figure 18. For the air compartment, the predicted concentrations of LOTOS-EUROS cover the measured European air concentrations of PCB-153 well. For that compartment, the concentration range in SimpleBox does not cover the lower measured concentrations. For the soil compartment, predicted concentrations in both LOTOS-EUROS and SimpleBox are up to 15 times lower than the highest measured concentrations, but cover the lower measured concentrations. In this case, the predictions of SimpleBox are closer to the measurements.

Maps of the concentration patterns in Europe in December 1985 are given in Figure 19. Figure 19a shows the spatial patterns in the air compartments of both models, and Figure 19b displays the soil concentrations. Figure 19a clearly illustrates that in SimpleBox, PCB-153 concentrations spread more evenly over



the calculation domain than in LOTOS-EUROS. Though, particularly in the air compartment, the maps show the same concentration 'hot spots'. Equal concentration hot spots can also be found on the soil maps, but due to equalization of the legends of the maps in combination with differences in absolute soil concentrations between SimpleBox and LOTOS-EUROS,

Figure 19: Spatial air concentration patterns of PCB-153 in December 1985 in µg.m^{-3}.
19a1: Air concentrations predicted by LOTOS-EUROS,
19a2: Air concentrations predicted by SimpleBox,
19b1: Soil concentrations predicted by LOTOS-EUROS,
19b2: Soil concentrations predicted by SimpleBox.

not all hot spots can be distinguished clearly on these maps.

Discussion

Air compartment

Average PCB-153 concentrations in air calculated by LOTOS-EUROS and SimpleBox differ at maximum a factor of two. Since the uncertainty in the emissions is assumed to be at least an order of magnitude (Breivik et al., 2002), the predictions of the two models can be considered comparable. Besides, both models predict concentrations that are in line with concentrations of PCB-153 measured in Europe. For the air compartment, the spatial concentration variance in SimpleBox is typically smaller than in LOTOS-EUROS and in the measured values. This is also illustrated by the maps with spatial concentration patterns, although both models do predict the same concentration 'hot spots'. The cause of the relatively small concentration range in the air compartment of SimpleBox is the averaging of regional and continental emissions, which leads to an averaged prediction of chemical inflow towards the considered cell. When a cell with high emission intensity is considered, the influence of the chemical inflow from surrounding cells on the concentration within that cell will be relatively small. Therefore, the concentrations in high-emission cells will be predicted more or less equally by SimpleBox and LOTOS-EUROS. However, when a cell with low emission intensity is considered, the relative influence of the inflow of chemicals from surrounding cells will be high. In those cases, LOTOS-EUROS yields more realistic predictions of the chemical inflow than SimpleBox does with its averaged regional circumstances of a 200 x 200 km area. This phenomenon is also illustrated in Figure 20, which shows that in case of high emissions, a much stronger correlation exists between the emissions and the air concentrations than in case of low emissions. This means that in low-emission cells, the influence of other factors than the emissions, such as advective inflow and outflow, is relatively large. Using the SimpleBox-method, the chemical inflow towards a low-emission cell is almost always overestimated, and so is the air concentration in that cell. This is caused by the fact that the air concentrations in the cells follow a lognormal distribution: on average the concentrations are relatively low, but there are a few cells with high peak concentrations. The average air concentration on the regional scale is strongly influenced by these peaks, which means that the 5th percentile of the lower concentration boundary in SimpleBox is higher than the lower measured concentrations and the LOTOS-EUROS predictions. This is the major disadvantage of calculating spatial concentration variances with a nested model like SimpleBox. However, from a policy point of view, it may be more important to predict the upper concentration boundaries correctly than the lower concentration boundaries. For PCB-153, this phenomenon only occurs clearly in the air compartment, since for that compound the chemical inflow by air is a relatively important chemical transport mechanism. In general, this phenomenon will appear strongest when chemical emissions occur towards the air compartment only, and when volatile or persistent chemicals are considered. Besides, when using the SimpleBox-method for calculating spatial

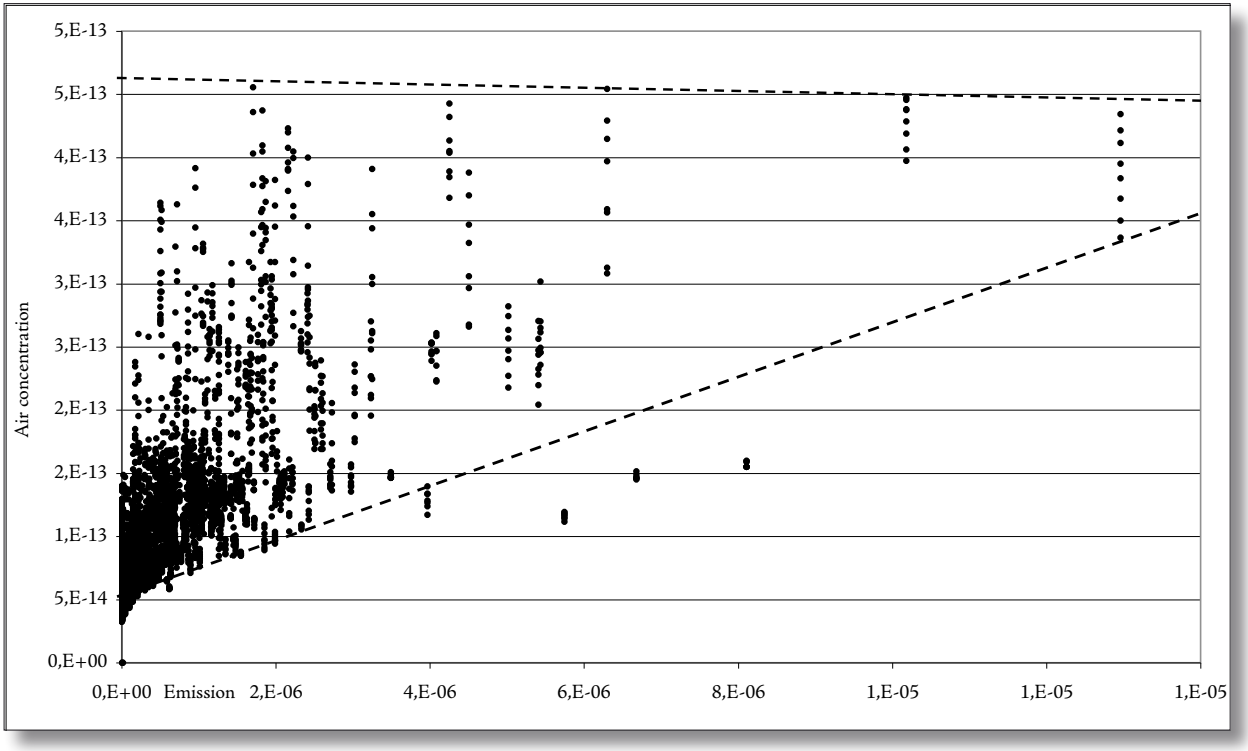


Figure 20: Correlation between the emissions and the air concentrations, calculated by SimpleBox for the 14,000 grid cells.

concentration ranges, smoothing spatial differences in concentrations will be higher when the local cell is smaller with respect to the regional and continental shell in which it is embedded.

Another factor causing differences in the air concentration predictions of LOTOS-EUROS and SimpleBox, is the presence of four atmospheric layers up to a height of 3500 m, between which vertical exchange is calculated following Yamartino et al. (2004). Within the atmospheric mixing layer, a surface layer with a thickness of 25 m is distinguished. SimpleBox distinguishes only one atmospheric mixing layer of which a fixed fraction of air is exported outside the system. Air concentrations in the models were compared for the atmospheric mixing layer only. The concentrations in LOTOS-EUROS are influenced by the vertical diffusion from the mixing layer to the surface layer and to the higher atmospheric layers and back. This leads to differences in concentration predictions in LOTOS-EUROS and SimpleBox. Besides, chemical transport

from air to soil vice versa is influenced by the presence of the atmospheric surface layer and a thin soil layer of 0.5 cm. However, these two phenomena only had a minor influence on the concentration differences with respect to the differences caused by the averaging of emissions on the regional and continental scales in SimpleBox.

Soil compartment

Average PCB-153 concentrations in soil calculated by LOTOS-EUROS and SimpleBox differ at maximum a factor of three. Also for this compartment, the discrepancy in model predictions is smaller than the uncertainty in the emissions solely, which implies that the model results are considered comparable. In the soil compartment, both models predict a concentration increasing from zero at the start of the calculation to 200 $pg.g^{-1}$ after eight years of calculation. This concentration progress is a modeling artefact that has to be ascribed to the fact that the calculations started with zero initial concentrations. The results are therefore not reliable for this period. Since, after some time, the concentrations reach a maximum level from which they only slightly decline until the end of the calculation period, it can be concluded that in the last part of the calculation, the initial concentration settings do not influence the model outcomes anymore. This means that for at least the last 12 years, the results can be considered reliable for the soil compartment. This is approved by the fact that the deviations between the spatial concentration variances of SimpleBox, LOTOS-EUROS and measured concentrations are at maximum one order of magnitude in the soil compartment.

The influence of surrounding cells on the concentration is much smaller in the soil compartment than in the air compartment, so the lower concentration boundary is predicted more accurately. The differences in the average soil concentrations and the spatial concentration ranges of both models are mainly caused by the fact that the soil compartment in LOTOS-EUROS is divided into five layers, while SimpleBox has one large soil box. This layered soil module of LOTOS-EUROS causes relatively high predictions of the amount of PCB-153 volatizing towards the air, resulting in systematically lower soil concentrations than predicted by SimpleBox.

Spatial and temporal patterns

Apart from the daily concentration fluctuations that are apparent in LOTOS-EUROS and not in SimpleBox, the models show similar temporal patterns in the air and soil compartments with concentration peaks at the same moments. The influence of the modeling time step, being three hours in LOTOS-EUROS and one month in SimpleBox, is only noticeable on the short time scale. The temporal concentration patterns in the air follow the trend in the emissions, while in the soil compartment there is an accumulation of PCB-153 during the first eight years of the calculation period due to atmospheric deposition. When the emissions decline, the amount of PCB-153 in the soil slightly decreases until the end of the calculation period, due to degradation and re-volatilization. The maps from the SimpleBox calculations give a similar picture of the spatial pattern of the PCB-153 concentrations in Europe as LOTOS-EUROS. However, since it is quite labour-intensive to derive these maps from a non-spa-

tial model, the use of a spatial model is recommended when one is interested in those spatial patterns.

The results show a peak in the concentrations of PCB-153 at the mid 1980s. During the calculation period of this study, this was the episode in which the highest emission intensities occurred. It should be taken into account that within a larger historical context, it is only a relative concentration peak. Sweetman et al. (2002) performed a study on the PCB-153 concentrations in soil and sediment in the UK in the period 1940-2000, and from their results, it can be concluded that the absolute emission and concentration peak for this compound occurred in the period 1960-1970. However, for the period 1981-2000, average PCB-153 concentrations in the soil compartment predicted by Sweetman et al. (2002) are in the same order of magnitude as those predicted by our study.

Model setup

Over all, this validation study of the spatial LOTOS-EUROS model shows positive results, as its predictions agree well with the average SimpleBox predictions and with field measurements. These findings agree with those of Hansen et al. (2006), who compared the multimedia box model EVn-BETR with the atmospheric model DEHM-POP. The method applied here to predict spatial concentration variances from a nested generic multimedia mass balance model performs adequately for PCB-153 in most cases, except for the lower concentration boundary in the air compartment. For risk assessment studies, the maximum concentrations are generally of more interest than the minimum concentrations. It can therefore be concluded that the SimpleBox-method can be used for predicting spatial average and peak concentrations in risk assessments for this specific chemical. Hereby, one should notice that for risk assessments, it is not desirable to run a model 14,000 times in order to derive spatial results. However, in many risk assessment studies, the total area under consideration is smaller than in our study and/or the spatial resolution is less detailed than 25 x 25 km. In cases less model runs will be needed to perform a calculation, the proposed method is appropriate.

For now, the only compound studied is PCB-153, and the only emission scenario is towards the air compartment. It is expected that different compounds will show different results, as do different emission scenarios. The same is the case when smaller or larger cells are considered with respect to the surrounding areas. Therefore, to give a more founded judgment of the usefulness of the method proposed here to predict spatial concentration variances from a non-spatial nested model, a systematic test for all types of compounds, emission scenarios, environmental compartments, and spatial scales is required. After such a study, it can be concluded whether the use of spatially resolved models, which calculate concentrations for each cell of a grid simultaneously, are significantly advantageous to predicting environmental concentrations. Or that for certain risk assessment purposes, nested multimedia models can be used as well. The challenge will be to develop general rules for groups of compounds and environmental circumstances for predicting spatial concentration variances with generic multimedia fate models.

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6 Estimating overall persistence and long-range transport potential of persistent organic pollutants

Seven multimedia mass balance models and atmospheric transport models in comparison

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Abstract

Two different approaches to modeling the environmental fate of organic chemicals have been developed in the recent years. The first is the multimedia partitioning approach, which is generally applied in multimedia box or mass balance models. The second approach is based on the atmospheric dynamics and is applied in atmospheric transport models. Ideally, both types of models would yield the same outcomes for descriptors of overall persistence (P_{ov}) and long-range transport potential (LRTP). The main goal of the present study was to investigate if the multimedia mass balance models ClimoChem, SimpleBox, EVn-BETR, G-CIEMS, OECD-tool and the atmospheric transport models MSCE-POP and ADEPT predict the same rankings of the P_{ov} and LRTP of POPs, and to explain differences and similarities between the rankings by the mass distributions and inter-compartment mass flows. The study was performed for a group of 14 reference chemicals. With respect to P_{ov}, the models yield consistent results, which means that phase partitioning and degradation rates are described similarly by all model types. Concerning LRTP, there are larger differences between the models than for P_{ov}, due to different LRTP-calculation methods and spatial model resolutions. Between atmospheric transport models and multimedia fate models, no large differences in mass distributions and inter-compartment flows can be recognized. Deviations in mass flows are mainly caused by the geometrical design of the models.

Introduction

Pollution caused by Persistent Organic Pollutants (POPs) is one of the large global environmental problems, due to the long environmental persistence of these substances and their ability to be transported over long distances. Historically, two different policy fields have been involved with POPs in the environment (i.e. air quality and chemical safety), and within each field an international convention on POPs was formulated. First, under the auspices of the United Nations Economic Commission for Europe (UN-ECE), the international community on air quality recognized the potential hazards of POPs, and within the framework of the Convention on Long-range Transboundary Air Pollution (CLRTAP, 1979; ECE/EB.AIR/50, 1996) 27 countries (as of 2007) ratified the Protocol on Persistent Organic Pollutants (ECE/EB.AIR/60, 1998). This Protocol encourages the research, emission reduction and monitoring of POPs, as well as the international co-operation between scientists. Second, the United Nations Environment Programme (UNEP), which focuses on chemical safety, described its policy on POPs in the Stockholm Convention (UNEP, 2001). In both fields, POP fate modeling is a relevant source of information. Mathematical models are increasingly used to simulate the environmental distribution of POPs (Scheringer and Wania, 2003; Gusev et al., 2005; Hansen et al., 2006), because there is only a limited amount of measurements available with a poor spatial and temporal coverage. Moreover, the use of models provides better insight in and understanding of the behavior of POPs in the environment. Accordingly the Executive Body of the CLRTAP, under its Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe initiated an inter-comparison study between different POP fate models, to which experts of different countries would contribute (EMEP; ECE/EB.AIR/75, 2002). The study presented in this paper is a result of a part of this model inter-comparison study.

Two different POPs fate modeling approaches have been developed in the recent years. The first is the multimedia partitioning approach, which is generally applied in multimedia box or mass balance models. This type of models assumes homogeneous environmental compartments, and due to their relatively low complexity, they are often used in risk assessments, i.e. for screening assessments of large numbers of chemicals. The classical well-mixed box models have little or no spatial resolution. In recent years, beside the box models, also spatially explicit multimedia mass balance models have been developed (i.e. IMPACT-2002, Pennington et al., 2005; BETR-Global, MacLeod et al., 2005; G-CIEMS, Suzuki et al., 2005). The second approach, developed from the air quality field, is based on the atmospheric dynamics, and applied in atmospheric transport models (i.e. Malanichev, 2004; Lammel et al., 2001). These types of models are spatially resolved models, generally providing a higher temporal and spatial resolution than box models.

Both types of models can be used for the same goal: to identify chemicals with POP-like persistence and long-range transport potential. Ideally, both types of models would yield the same outcomes for descriptors

of overall persistence (P_{ov}) and long-range transport potential (LRTP). However, only few studies have investigated this question and it is not sufficiently clear how consistent the different models are. First, the different spatial and temporal resolutions used may lead to differences in model predictions. Second, different models of the same type may predict different concentrations and process intensities owing to variation in model algorithms and geometric dimensions. The following aspects have been addressed in recent model comparison studies: a number of spatially explicit models have been compared with non-spatial versions of the same model domain (Armitage et al., 2007; e.g. Klepper and den Hollander, 1999; Pennington et al., 2005). Wania and Dugani (2003) compared the LRTP estimates of polybrominated diphenyl ethers for four multimedia fate models. Fenner et al. (2005) performed a model inter-comparison study on the predicted P_{ov} and LRTP of chemicals for nine multimedia fate models. However, these studies did not take into account atmospheric transport models. Hansen et al. (2006) explored the differences in predicted concentrations of α-HCH between an atmospheric transport model and a multimedia mass balance model. They compared EVn-BETR with DEHM-POP, and related the predicted concentration differences to the differences in the model description of environmental processes in the two models. Hollander et al. (2007) compared average concentrations and spatial concentration patterns of PCB-153 between the atmospheric model LOTOS-EUROS and the multimedia mass balance model SimpleBox for PCB-153. In these two studies, only one single multimedia model and one atmospheric model were taken into account, which makes it difficult to make general statements on the performance of the two model types. Lammel et al. (2007) presented a comparison study between the multimedia models SimpleBox 2.0 (Brandes et al., 1996), Chemrange 1.0 (Held, 2001; Scheringer et al., 2001), MPI-MBM (Lammel, 2004) and the atmospheric transport model MCTM (Lammel et al., 2001; Semeena and Lammel, 2003; Semeena et al., 2005) for six substances. Although they found deviations between the models for the quantification of the LRTP of these compounds, they concluded that there is good agreement between the models with respect to the LRTP-ranking of chemicals.

The main goal of the present study is to investigate if the multimedia mass balance models ClimoChem (Scheringer et al., 2000), SimpleBox (Den Hollander et al., 2004), EVn-BETR (Prevedouros, 2004), G-CIEMS (Suzuki et al., 2005), OECD-tool (Scheringer et al., 2006) and the atmospheric transport models MSCE-POP (Gusev et al., 2005) and ADEPT (Roemer et al., 2004) predict the same rankings of the P_{ov} and LRTP of POPs. The second goal is to explain differences and similarities between the rankings of the different models by the mass distributions and inter-compartment mass flows.

Material and methods

Model setup

Seven models for predicting POP's environmental fate participated in this inter-comparison study, of which two are derived from atmospheric transport models

(ADEPT and MSCE-POP). The other five models are based on a multimedia mass balance modeling approach (i.e. EVn-BETR, SimpleBox, G-CIEMS and ClimoChem, OECD-tool). The models show a wide variety in their spatial resolutions. In the comparison of P_{ov} and LRTP rankings, all models were taken into account, whereas the mass balance analysis was performed for five of seven models (not for ADEPT and the OECD-tool). A brief description of the participating models is given in Appendix D2, and a schematic presentation of the key features of each model is given in Shatalov et al. (2004).

The study was performed for the calculation domain covering the area of 35°-70° N and 10° W-30° E, which represents Europe and some parts of North-Africa and the North Atlantic and Arctic oceans. For this area, spatially explicit environmental data on a 1°x1° scale, for which the same datasets were used by all models, were used for land cover data, leaf area indices and organic matter contents in the soil. Land cover data were derived from the USGS Land Use/Land Cover dataset obtained from the NCAR Mesoscale Modeling System (MM5; Guo and Chen, 1994). The 25 specified categories of the original land cover database were aggregated to the number of land cover classes that were distinguished in each model (i.e. three classes in ClimoChem, six in MSCE-POP, five in SimpleBox). Leaf area indices were derived from Sellers et al. (1994) and organic matter contents in soil were obtained from NASA (2004). The spatially explicit environmental input data were assumed to be constant in time during the calculation period. Beside these data, each model used its own additional environmental parameter input. Information on the environmental input parameters used by each individual model can be found in Shatalov et al. (2004).

P_{ov} and LRTP estimates

Each model was used to provide an estimate of P_{ov} and LRTP for a group of 14 reference POP-chemicals, and to derive rankings from high to low P_{ov} and LRTP. P_{ov} and LRTP are environmental hazard metrics, which are often applied in risk assessments of chemicals. The selected chemicals were aldrin, atrazine, B[a]P, BDE-47, BDE-99, biphenyl, CCl_4, HCB, HCBD, α-HCH, p-cresol, PCB-180, PCB-153 and PCB-28. Their physical-chemical properties are given in Appendix D1. The emission scenario used in the calculations was a single pulse point source located at 10°E and 52.5°N, followed by a no-emission simulation period of one year.

Each of the models used its own method to calculate P_{ov} and LRTP, due to differences in the construction of the models. Although defined slightly different in the different models, P_{ov} largely reflects the turn-over time of the chemicals in the chosen model system. LRTP was also defined differently in the models. The method for the calculation of P_{ov} and LRTP in each of the models is given in Table 8. It was not possible to calculate P_{ov} in ADEPT, because, since ADEPT is a diagnostic and not a prognostic tool, the model has no time-dimension. In the OECD-tool, LRTP was calculated with two different methods, see Table 8. Rank correlation coefficients between the rankings of the 14 chemicals obtained with the different models were calculated (Hogg and Craig, 1995).

	MSCE-POP	*CliMoChem*	*SimpleBox*	*EVN-BETR*	*G-CIEMS*	*ADEPT*	*OECD-tool*
P_{ov}	*Inverse value of the weighted mean of degradation rate constants in the environmental media atmosphere, soil, seawater, vegetation, sediments (weights: fractions of a pollutant accumulated in these media during the simulation time)*	*Time-integrated mass in the entire model system divided by amount initially released.*	*The point of time at which the initial mass emitted to the model domain (M0) is reduced to 1/e*M0*	*The time taken for the initial mass emitted to the model domain to be reduced by half.*	*The fraction of the amount released that remains in the specified model domain after the simulation period.*	*no P_{ov} calculated*	*Overall residence time of the chemical in the entire model system (mass at steady state divided by release rate).*
LRTP	*TD: transport distance defined as the average distance from the source at which the mean annual atmospheric concentration of a chemical is 1000 times lower than the concentration near the point source (Rodan et al., 1999).*	*Fraction of amount released that is transported to the Arctic and remains there, i.e. time-integrated net flux into the Arctic divided by M0.*	*The fraction of the amount released that is exported over the boundaries of the model domain at the end of the simulation period*	*The average distance from a point source at which the chemical's concentration has dropped to 38% of its initial concentration (1/e*M0)*	*The cumulative fraction of a substance transported by advection out of the air compartment of the model domain during the simulation period*	*The distance from a point source in easterly direction at which the chemical's concentration has dropped to 38% of its initial concentration (1/e*M0)*	*CTD: the distance from a point source at which the chemical's concentration has dropped to 38% of its initial concentration. TE: transport efficiency is the percentage of emitted chemical that is deposited to surface media after transport away from the region of release.*

Table 8: Calculation methods for P_{ov} and LRTP in the different models.

Mass balance estimates of PCB-153

In order to explain differences and similarities between the rankings of the different models, mass distributions and inter-compartment flows were investigated for one example compound. This analysis of mass balances was performed for PCB-153 because emission are available for this compound and because it is a 'multimedia chemical', which means that after emission, it is distributed among different environmental compartments. The physical-chemical input data of PCB-153 are given in Table 9. Yearly averaged PCB emission data for the period 1981 to 2000 were derived from Breivik et al. (2002) on a 1°x1° scale and

Parameter	*Value*	*Unit*	*Reference*
Molecular weight	$3.61*10^{+2}$	$g \cdot mol^{-1}$	*Mackay et al., 1992*
Vapor pressure at 25°C	$8.82*10^{-5}$	*Pa*	*Li et al, 2003*
Water solubility at 25°C	$6.50*10^{-3}$	$mg \cdot l^{-1}$	*Li et al, 2003*
K_{ow}	$1.45*10^{+7}$	-	*Li et al, 2003*
Gas/water partition coefficient at 25°C	$2.09*10^{-3}$	-	*Li et al, 2003*
Solids/water partition coefficient at 25°C	$2.96*10^{+5}$	-	*Li et al, 2003*
Enthalpy of vaporization	$8.77*10^{+1}$	$kJ \cdot mol^{-1}$	*Li et al, 2003*
Enthalpy of dissolution	$2.50*10^{+1}$	$kJ \cdot mol^{-1}$	*Li et al, 2003*
Gas phase degradation rate constant at 25°C	$3.50*10^{-8}$	s^{-1}	*Mackay et al., 1992*
Dissolved phase degradation rate constant at 25°C	$3.50*10^{-9}$	s^{-1}	*Mackay et al., 1992*
Bulk degradation rate constant sediment at 25°C	$3.50*10^{-9}$	s^{-1}	*Mackay et al., 1992*
Bulk degradation rate constant soil at 25°C	$3.50*10^{-9}$	s^{-1}	*Mackay et al., 1992*

Table 9: Physical-chemical input data for PCB-153.

converted to grid-format as described by Shatalov et al. (2006). The models were run for the period 1981-2000 with time intervals of one month for SimpleBox, EVn-BETR, G-CIEMS and MSCE-POP, and three months for ClimoChem.
Masses and concentrations of PCB-153 were recorded at the end of the year 2000 for air, water, and soil. Mass flows between the compartments were calculated and similarities and discrepancies between the models were analyzed. When possible, differences between the individual models were traced back to general differences between (spatially explicit) multimedia mass balance models and atmospheric transport models.

Results

P_{ov} and LRTP rankings of chemicals

In Figure 21, the relative rankings of the 14 selected POPs according to their overall persistence are given for the six models. A value of 1 represents the lowest P_{ov} and a value of 14 the highest P_{ov}. There is agreement between the models with respect to the P_{ov} rankings to the extent that the individual models in most cases differ by only one or two scores from the average ranking. The largest deviations of individual compound rankings can be found for HCBD, PCB-153, and PCB-180 in EVN-BETR. The mean divergence from the average ranking is 0.69. The correlations of the P_{ov} rankings among the individual models are given in Table 10. The lowest correlation coefficient has a value of 0.81, which confirms the consistency of the P_{ov} rankings. The mean deviation from the average ranks is smallest for MSCE-POP, G-CIEMS, and

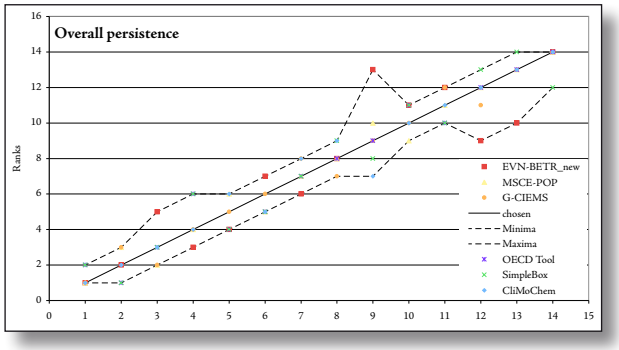

Figure 21: Relative rankings of the 14 selected test chemicals according to their overall persistence (P_{ov}) for six models (ADEPT does not yield P_{ov}). The value 1 represents the lowest P_{ov} and the value 14 the highest P_{ov}. The solid line shows the average ranking of the chemicals for all models together. The dashed lines show the minimum and maximum rankings of the chemicals 1=p-cresol, 2=aldrin, 3=biphenyl, 4=atrazine, 5=BaP, 6=PCB-28, 7=α-HCH, 8=BDE-47, 9=HCBD, 10=BDE-99, 11=HCB, 12=PCB-153, 13=PCB-180, 14=CCl4.

	ClimoChem	*EVN-BETR*	*MSCE-POP*	*SimpleBox*	*OECD-Tool*	*G-CIEMS*
ClimoChem	*1*	*0.84*	*0.97*	*0.96*	*0.96*	*0.97*
EVN-BETR		*1*	*0.89*	*0.81*	*0.87*	*0.89*
MSCE-POP			*1*	*0.93*	*0.96*	*0.98*
SimpleBox				*1*	*0.98*	*0.93*
OECD-Tool					*1*	*0.96*
G-CIEMS						*1*
Average	*0.99*	*0.9*	*0.99*	*0.96*	*0.98*	*0.99*

Table 10: Rank correlations between the individual models according to their P_{ov} rankings. The bottom line shows the correlation between each model and the average ranking of all models together.

CliMoChem (0.43 scores). p-Cresol and CCl_4 are the chemicals with the most consistent rankings by all models; HCBD received the most diverse scores in the different models.

Figure 22 shows the relative rankings of the 14 selected POPs according to their long-range transport potential (LRTP). There is less agreement between the models according to the LRTP rankings than according to the P_{ov} rankings. For LRTP, the individual models at maximum differ by seven scores from the average ranking, whereas the mean divergence from the average ranking is 1.4. The correlations according to the LRTP rankings between the individual models are given in Table 11. The lowest correlation coefficients are observed for CliMoChem because the LRTP metric used in CliMoChem is conceptually different from the other LRTP metrics, see Discussion section. If CliMoChem is excluded, the lowest correlation coefficient is 0.57 (ADEPT vs. EVn-BETR). The mean deviation from the average ranks is smallest for the OECD Tool (0.7 and 1.0 scores); CliMoChem and ADEPT show the largest deviations (2.4 and 2.0 scores, respecitvely). The low-LRTP chemicals aldrin, p-cresol and BaP exhibit the most consistent rankings among all models (mean deviation from average rank around 0.5 scores); PCB-180, PCB-28 and α-HCH are ranked most differently by the different models (mean difference from average rank around 2 scores).

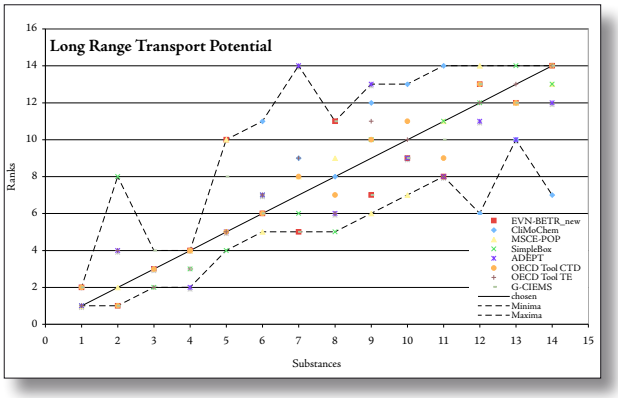

Figure 22: Relative rankings of the 14 selected test chemicals according to their long-range transport potential (LRTP) for the seven models. The value 1 represents the lowest LRTP and the value 14 the highest LRTP. The solid line shows the average ranking of the chemicals for all models together. The dashed lines show the minimum and maximum rankings of the chemicals.
1=aldrin, 2=atrazine, 3=p-cresol, 4=BaP, 5=biphenyl, 6=BDE-47, 7=BDE-99, 8=PCB-28, 9=PCB-180, 10=PCB-153, 11=α-HCH, 12=HCBD, 13=HCB, 14=CCl4.

	CliMoChem	*EVN-BETR*	*MSCE-POP*	*SimpleBox*	*ADEPT*	*OECD-tool CTD*	*OECD-tool TE*	*G-CIEMS*
CliMoChem	1	0.44	0.45	0.55	0.64	0.64	0.62	0.52
EVN-BETR		1	0.93	0.67	0.57	0.86	0.78	0.98
MSCE-POP			1	0.72	0.65	0.85	0.79	0.93
SimpeBox				1	0.74	0.83	0.91	0.73
ADEPT					1	0.83	0.9	0.6
OECD-tool CTD						1	0.96	0.89
OECD-tool TE							1	0.81
G-CIEMS								1
Average	0.67	0.88	0.89	0.88	0.78	0.97	0.94	0.93

Table 11: Rank correlations between the individual models according to their LRTP rankings. The bottom line shows the correlation between each model and the average ranking of all models together.

Masses of PCB-153 and inter-compartment fluxes

The mass flows of PCB-153 at the end of 2000 are given as percentage of the emission in Figure 23, for , MSCE-POP, ClimoChem, SimpleBox, EVn-BETR and G-CIEMS, respectively. In the grey boxes, the mass fractions of the chemical in the air, water and soil are given. A Table with the mass balance estimates of all five models is given in Appendix D4. Absolute concentrations of PCB-153 in air range from 0.44 $pg.m^{-3}$ in ClimoChem to 7.5 $pg.m^{-3}$ in EVn-BETR, and the masses in 2000 range from 27 kg in ClimoChem to 107 kg in MSCE-POP. Concentrations in water range from 0.2 $pg.l^{-1}$ in G-CIEMS to 2.0 $pg.l^{-1}$ in SimpleBox, and soil concentrations lie between 12 $pg.g^{-1}$ in ClimoChem and 63 $pg.g^{-1}$ in G-CIEMS. MSCE-POP only predicts the concentration at the interface between soil and air, which for PCB-153 is 168 $pg.g^{-1}$ in 2000. Figure 23 shows that in all models nearly the total mass of PCB-153 is present in the soil compartment, ranging from 95% in MSCE-POP and EVn-BETR to 99% percent in G-CIEMS. Only a small fraction is present in the air, and 0.4% (G-CIEMS) to 3.6% (SimpleBox) resides in the water compartment.

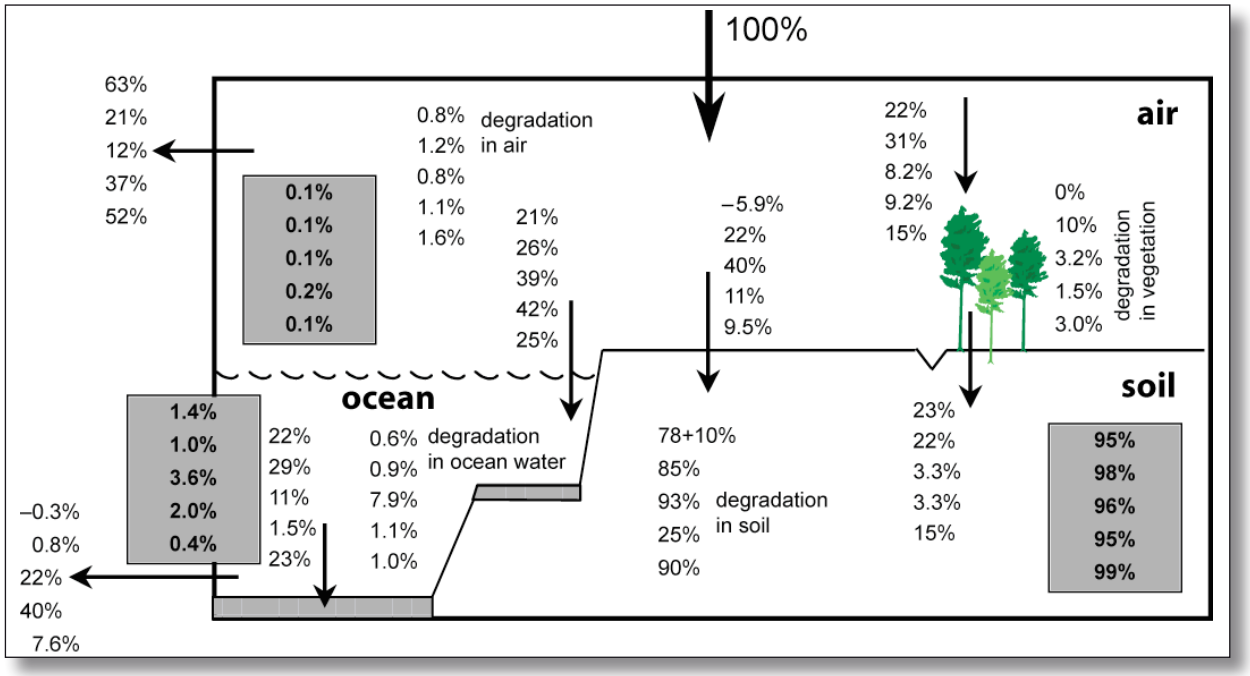

Figure 23: Calculated mass flows of PCB-153 in 2000 as percentage of the emission. In the grey boxes, mass fractions of the chemical in air, ocean water and soil are given. From top to bottom: MSCE-POP, ClimoChem, SimpleBox, EVn-BETR, G-CIEMS.

The predicted mass flows of PCB-153 between the air, water and soil compartments, and the net export flows are more different for the different models than the relative mass fractions. Large differences between the models occur in the export flow with air and water out of the model domain. MSCE-POP and G-CIEMS predict a high export flow from the air compartment (63%, resp. 52% of the emission of the year 2000 versus 12%-37% for the other models). In SimpleBox and EVn-BETR the export flow from the water compartment is relatively important (22%-40% for SimpleBox and EVn-BETR versus -0.3%-7.6% for MSCE-POP, G-CIEMS and ClimoChem). The fraction degraded in water is relatively large in SimpleBox.

The total fractions of atmospheric deposition, as well as the deposition to soil, water and vegetation, are given in Figure 24 for the different models. In 2000, all models except MSCE-POP show a net deposition flow from air to soil, with the largest flow for SimpleBox (40%), In MSCE-POP, a net volatilization flow of 5.9% is obtained. Deposition to vegetation is largest for ClimoChem and MSCE-POP, and consequently, the mass flow from vegetation to soil is also relatively

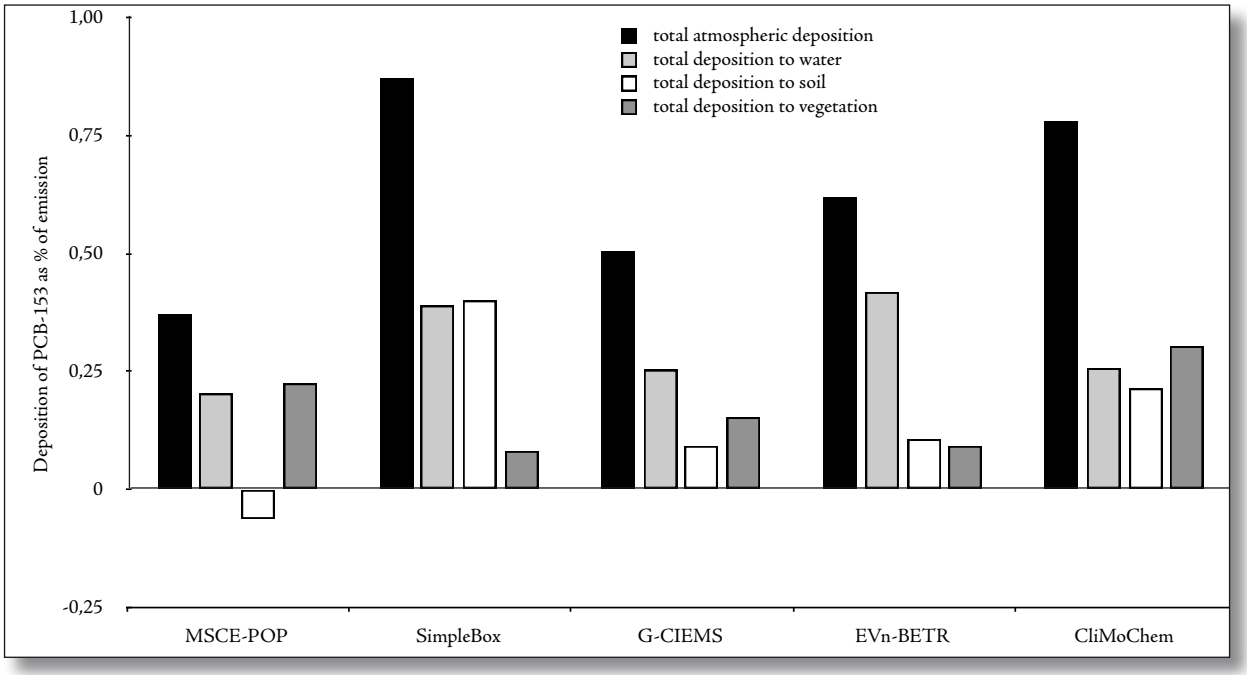

Figure 24: Predicted amounts of atmospheric deposition of PCB-153 to soil, water and vegetation for MSCE-POP, ClimoChem, SimpleBox and G-CIEMS. The amount of atmospheric deposition is given as percentage of the emission.

large in these models. In ClimoChem, a large fraction of the emitted PCB-153 is degraded in vegetation. MSCE-POP does not take into account this process in its model algorithms. In EVn-BETR, a relatively small fraction (25%) of the emitted substance is degraded in the soil. MSCE-POP distinguishes degradation in the litter layer (10% of the emitted PCB-153) and degradation in the soil (78% of the emissions), which was summed up as total soil degradation for this comparison study.

Discussion

P_{ov} rankings of chemicals

With respect to P_{ov}, the models are highly correlated. This means that not only degradation rate constants but also phase partitioning is described similarly in all models. The half-lives of a chemical in a given environmental medium can be expected to be similar in all models, because the models use the same input values (valid for 298 K) and adjust these values to temperatures different from 298 K in a similar way. In addition to the degradation half-lives, the distributions between air, water and soil influence P_{ov}. This distribution depends on the partition coefficients of the chemical and on the relative sizes of the differ-

ent environmental media, i.e. the model geometry. The good agreement for P_{ov} indicates that also phase partitioning is relatively similar in the models. Another possible cause of differences between the P_{ov}-rankings is the way of calculating P_{ov}. The most essential difference between the calculation methods is that some methods only consider degradation as a process determining persistence ('closed models'; i.e. MSCE-POP, ClimoChem), whereas others also take into account advective removal from the model domain ('open models'; i.e. SimpleBox, G-CIEMS). However, this may affect mainly absolute P_{ov}-values – absolute values may be lower in open models – but if the open and closed models yield similar fractions in air, the higher rate constant in air applies to all chemicals and does not strongly affect the ranking. Good agreement among models on their P_{ov} (and LRTP) estimates was also recognized by Fenner et al. (2005) for nine multimedia mass balance models and Lammel et al. (2007) for the atmospheric transport model MCTM and the multimedia mass balance models SimpleBox 2.0, Chemrange 1.0 and MPI-MBM.

LRTP rankings of chemicals

Concerning LRTP, there are larger differences between the models than for P_{ov}. First, this is caused by differences in the calculation methods. The strongest effect of this kind is observed for CliMoChem: LRTP in CliMoChem is calculated as the fraction of chemical that reaches the Arctic and remains there. Therefore, volatile chemicals such as CCl_4 and HCB, which receive high LRTP scores in all other models, have low scores in CliMoChem because they reach the Arctic but only a small fraction is deposited there whereas a large fraction is transported further. Second, the influence of import/export fluxes, which are modeled differently in models with different spatial resolution (Hansen et al. (2006)), is larger on LRTP than on P_{ov}. This is illustrated by the high correlations between the more highly resolved models MSCE-POP, G-CIEMS, and EVN-BETR, on one hand, and between the box models SimpleBox and OECD Tool, on the other hand. Besides spatial resolution, the presence of a deep ocean compartment, which acts as a sink for POPs, is an important factor. Deposition of chemical to the deep ocean reduces the predicted LRTP, whereas in absence of this process, an export flow out of the water compartment is modeled. In general, model geometry thus influences the LRTP estimates and rankings more strongly than the P_{ov}-rankings.

Masses of PCB-153 and inter-compartment fluxes

The five models taken into account in this mass balance study yield similar values for the predicted mass fractions in air, water and soil. In all models, the soil is the main storage compartment for PCB-153. During the emission period, a significant part of the substance was deposited onto the soil, and due to the low degradability of PCB-153, it accumulated there, resulting in a large reservoir in the soil. Emissions were declining during the last years of the calculation period. As a result, MSCE-POP predicts a volatilization flux from soil to air in the year 2000. In the other models, still a net deposition flux is calculated. Due to the large air-based export flux of PCB-153 out of the model system in MSCE-POP, the flux from soil to air is enhanced. Besides, MSCE-POP models a detailed vertical resolution in soil concentrations, resulting in relatively

high soil concentrations predicted in the upper soil layer.

The export of PCB-153 by air out of the considered domain is significantly lower in the box models SimpleBox and ClimoChem (12%, resp. 21%) than in the spatially explicit models EVn-BETR, MSCE-POP and G-CIEMS (37%, resp. 63% and 52%). Due to the higher spatial resolution, air concentrations in the border grid cells of the spatially explicit models domain are different from the average concentrations calculated by SimpleBox or ClimoChem. At the Northern borders of the model domain, the air concentrations are low, but at the Southern and Eastern borders, they are significantly higher than the average air concentrations from the total model area, resulting in a larger export flow of PCB-153 in the South and East. For EVn-BETR, to a certain extent we can see the same phenomenon as for MSCE-POP and G-CIEMS, but due to the coarser model scale, the effects on the total export flow are less pronounced than for MSCE-POP. In this model, export by air is a factor 1.5 to 2 lower than in MSCE-POP and G-CIEMS, but a factor 3 higher than in SimpleBox. A deviation between atmospheric transport models and multimedia mass balance models in predicted transport flows in air was also recognized by Lammel et al. (2007). They showed a tendency of box models to overestimate particle deposition from air and to underestimate atmospheric transport velocity due to neglecting the temporal and spatial variability of these parameters. The same phenomenon can be seen from the current inter-comparison study. The third factor causing differences in the fraction of PCB-153 that is exported is the atmospheric height applied in the models. MSCE-POP uses an atmospheric height of 12000 m, while SimpleBox only models the lower 1000 m of the atmosphere. From the current study, it appears that the larger the modeled atmospheric height, the larger the export of PCB-153 via air. This is in agreement with Wania and Dugani (2003), who concluded that a larger atmospheric mixing height strongly increases the predicted LRTP of PBDEs. For ClimoChem, model geometry strongly influences the export flow in a fourth way. In this model, the considered region falls within two latitudinal zones of the model that have no boundaries in East and West directions, which means that only export in Southward and Northward directions is counted as net export in ClimoChem. The lack of East and West borders in ClimoChem also influences the absolute emissions, masses and concentrations of PCB-153 in the media; these are 5 to 7 times respectively 2 to 10 times lower in ClimoChem than in the other models. All models indicate a net loss of PCB-153 between 1999 and 2000; 4000-5200 tonnes in MSCE-POP and SimpleBox and 445 tonnes in ClimoChem, which again reflects the lower emissions and amounts discussed above. The net loss in EVn-BETR is lower than in the other models (except ClimoChem), caused by a relatively small amount of PCB-153 degraded in soil. This can be explained by the relatively high contribution of air and water advection as loss processes in this model.

Export of PCB-153 from the model domain by water is relatively large in EVn-BETR and SimpleBox, and low in MSCE-POP and ClimoChem. On the other hand, in the latter models, a chemical flow from the surface

water sea to the deep ocean is included, which is lacking in the two former models. The sums of export and deep ocean flows in MSCE-POP and ClimoChem equal the export flows in EVn-BETR and SimpleBox, which explains the differences in the models when only export flows are compared.

The total amount of PCB-153 that is deposited to water is similar in all models (ranging from 21% to 42% of the amount released). Deposition to vegetation is similar and relatively high in MSCE-POP and ClimoChem, whereas it is similar and relatively low in SimpleBox and EVn-BETR. These differences can be fully traced back to the assumed values of the mass transfer coefficient at the air/vegetation interface. The total deposition flux from air is high in the multimedia box models (SimpleBox, EVn-BETR, ClimoChem) and clearly lower in the atmospheric model MSCE-POP.

Precipitation is described as meteorology-driven events in MSCE-POP, whereas in the multimedia models, a constant precipitation flux is assumed, leading to higher estimation of the wet deposition flux in these models. These outcomes are in agreement with the comparison of DEHM-POP and EVn-BETR (Hansen et al., 2006) and with Lammel et al. (2007). Lammel et al. (2007) suggest that dry particle deposition is also overestimated in multimedia mass balance models, first by assuming a constant and too low OH-radical concentration (Lammel, 2004). Second, these models usually use a dry deposition velocity corresponding to particle sizes close to the median mass size of aerosols (ca. 3 μm; Mackay, 2001), while the mass size distribution of semi-volatile substances is expected to follow the surface size distribution of aerosols, which peaks between 0.2 μm and 1 μm (Jaenicke, 1988).

Multimedia mass balance models vs. atmospheric transport models

From the analysis of the individual model differences, some general findings on differences between atmospheric transport models and multimedia mass balance models, either spatially explicit or box models can be drawn. One factor causing differences in model results are differences in the way how the chemical transport processes are modeled. Another relevant factor is the geometrical design of the models. This second factor mainly influences export of substances out of the model domain by air transport, whereas differences in process descriptions (first factor) have the largest effect on the air-vegetation and air-soil exchange, as well as on the degradation rates in the water compartment. The deviation in predicted transport flows in air between atmospheric transport models and multimedia mass balance models was also recognized by Lammel et al. (2007). Because the influence of the spatial resolution is relatively important for export mass fluxes and LRTP, it seems that the largest differences exist between non-spatial (box) models and spatially explicit models, independent of whether these are spatial multimedia mass balance models or atmospheric transport models. At least for the scenario used in this study, differences in model algorithms and the way inter-compartment processes are described are subordinate to whether the model is a gridded model or not. In general, this phenomenon will appear strongest in model scenarios with a heterogeneous spatial emission pattern such as used here (one single point

source, which is the most heterogeneous emission pattern), causing different predictions of export flows of chemicals between the different models.

When choosing an appropriate model for analyzing the environmental fate of POPs, either a spatial vs. non-spatial model or an atmospheric transport model vs. a multimedia mass balance model, one should take into account several factors. First, the environmental compartment(s) in which one is interested is/are of importance. Air concentrations in an open model system are predicted more reliably by spatially explicit models due to their higher resolution, and even more by atmospheric transport models, due to their more accurate description of meteorological parameters and processes. For the less mobile media, particularly soils and sediments, the influence of model geometry on the calculated concentrations is much smaller. Besides, soil-related process descriptions usually do not differ much between multimedia mass balance models and atmospheric transport models. The second and most important factor determining the choice for a spatial or non-spatial model is the variation in emission intensities over the study area, since the emission pattern of compounds largely determines the concentration pattern (Pennington et al., 2005; Sweetman et al., 2002). If the emissions of a compound are highly heterogeneous within the study area, and the influence of this heterogeneity is to be evaluated by the model, a spatially explicit model has to be used to determine the environmental concentrations. In contrast, if the emissions are more evenly distributed or if one is only interested in average concentrations over a larger area, the results of non-spatial models are satisfactory. The same applies to the ranking of chemicals according to their overall persistence and long-range transport potential. There are only some minor differences between spatial and non-spatial models and between atmospheric transport models and multimedia mass balance models, which are mainly caused by differences in the calculation methods of P_{ov} and LRTP. The practical reason to choose for multimedia mass balance models remains their simplicity of use. When large numbers of substances are to be processed, the use of more demanding atmospheric transport models may be impractical.

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7 Substance or space?

The relative importance of substance properties and environmental characteristics in modeling the fate of chemicals in Europe

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Abstract

The environmental fate of any chemical is controlled by two main factors: the properties of the chemical itself and the characteristics of the environment. The classical box approach in multimedia mass balance models assumes that chemical properties largely determine the fate of substances in the environment. In this study, the relative influence of substance properties and of environmental characteristics on the variation in concentrations of chemicals in Europe was compared for nine emission/receiving compartment scenarios. This was done for a combination of 200 randomly selected organic chemicals and 137 realistic European regions, representing a 250x250 km spatial scale. Stepwise multiple regression analysis was performed to determine the contribution of each of the individual input parameters on the total concentration variation. Depending on the scenario, the range in predicted environmental concentrations spreads from 2 up to 9 orders of magnitude. The assumption that the variation in the fate of chemicals in the environment mainly depends on substance-specific partition coefficients and degradation rates, appeared to be valid. For the estimation of soil and water concentrations with direct emissions to these compartments, however, the influence of spatial variation in environmental characteristics should not be neglected in multimedia mass balance models.

Introduction

The environmental fate of chemicals is controlled by two main factors: the properties of the chemical (e.g. vapor pressure, water solubility, degradation half-lives) and the characteristics of the environment (e.g. temperature, soil organic carbon content, OH-radical concentration). At equal release rates, concentrations may diverge for different chemicals and for different environments (Webster and Mackay, 2003). Multimedia mass balance models (box models) are often used to predict the environmental fate of chemicals for regulatory purposes, e.g. in comparative risk assessments. The classical box model (Mackay and Paterson, 1981; Mackay et al., 1982) approach implicitly assumes that chemical properties largely determine the fate of substances in the environment. In these models, chemical-to-chemical differences in model outcomes are met by the requirement of physical-chemical input data of the studied compounds. However, the possible role of the environmental characteristics are disregarded by limiting the analyses to modeling 'typical' or 'average' conditions only. By focusing on the chemical properties, the possible importance of the environmental characteristics may be underestimated. Does it suffice for environmental risk assessments of chemicals to take account of the substance that is released, neglecting the potential role of the local environmental conditions? How well do we know the relative contribution of substance properties and environmental characteristics to the fate of chemicals?

The traditional way to account for spatial variation in environmental characteristics is the use of spatially resolved models. In the last few years, a number of such spatial multimedia models have been developed (Pennington et al., 2005;, Prevedouros et al., 2004; MacLeod et al., 2005; Suzuki et al., 2005; Cahill and Mackay, 2003). Unfortunately, spatially explicit model outputs can only be derived at the rate of an increased model complexity and input data demand, whereas 'low-complexity' and 'easy-to-use' models are still desirable, particularly for screening assessments of large numbers of chemicals. To determine whether a spatially resolved model is necessary, information is required on the spatial variation of the environmental input data and of the influence of that spatial variation on the model results.

Several authors have explored this issue for single landscape characteristics. Sweetman et al. (2005), for example, examined the role of soil organic carbon in the global cycling of POPs, and Wania and McLachlan (2001) estimated the influence of forest characteristics on the overall fate of semi-volatile organic chemicals. Furthermore, sensitivity analyses have been performed on both physical-chemical properties and on landscape characteristics in multimedia mass balance models (Hertwich et al., 1999; Maddalena et al., 2001; MacLeod et al., 2002), and regional differences in multimedia model outcomes were explored (Webster et al., 2004). MacLeod et al. (2002) proposed a method to perform Monte Carlo analysis as a starting point for identification of sensitive model inputs. However, none of these studies have systematically addressed the relative importance of the real spatial variation in the total set of environmental characteristics compared to the differences in substance properties.

The objective of this study is to systematically estimate the influence of the spatial variation in environmental characteristics in Europe on the variation in environmental concentrations of chemicals and to compare it with the variation caused by differences in chemical characteristics. The study was performed for 200 organic chemicals, covering the domain of plausible chemical properties, combined with a set of 20 European environmental parameters on a 250x250 km scale. Calculations were performed for three emission scenarios, i.e. towards the air, water and soil compartments, respectively. The results were analyzed for the receiving compartments air, water and soil. Emission intensities were set invariant for the purpose of this study. The contribution of each of the individual parameters on the total concentration variation was examined using stepwise multiple regression analysis.

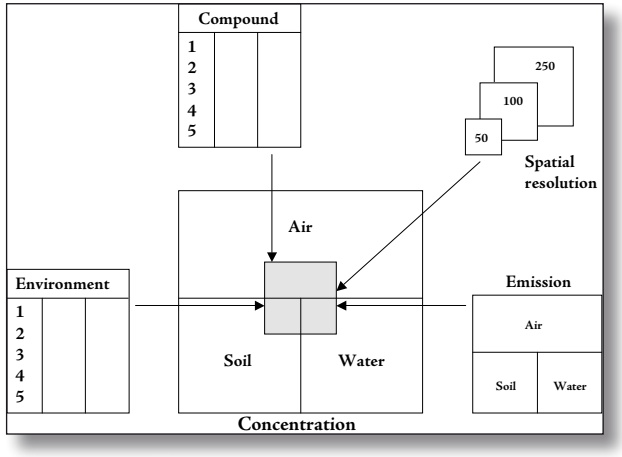

Figure 25: Schematic setup of the model study showing the different types of input parameters taken into account in the study. The gray block represents the regional cell to which emissions take place and in which environmental concentrations are estimated.

Methods

Model setup

Concentration predictions were performed with a nested multimedia mass balance model, of which a 250x250 km scale cell was parameterized successively for the different regions of Europe, each with its own characteristic set of environmental conditions. A nested model was used in order to include the exchange of chemicals between the regional cell and the surrounding areas. To this end, a 250x250 km scale cell was implemented in the level III multimedia model BasinBox (Hollander et al., 2006), which is based on SimpleBox 3.0 (Den Hollander et al., 2004). The default model settings in BasinBox were applied, except that the upstream, midstream and downstream areas were aggregated. The cell consisted of an air, soil, water, sediment and vegetation compartment. Figure 25 presents a schematic setup of the model study. Results were obtained for each individual region, for emissions to respectively air, soil and water with a unit emission, and corresponding concentrations were compared. Emission was set to take place to the nested cell only.

To parameterize the regional scale cells, a dataset was created containing realistic property combinations of 20 environmental parameters in Europe (Table 12). Histograms showing the range in parameter values are given in Appendix E2. These parameters correspond to the input requirements for the spatially distributed

Environmental parameter	*Code*	*Unit*	*Reference*
Surface water depth	*D*	*m*	*Pistocchi and Pennington, 2006*
Soil erosion intensity	*EROS*	$mm.y^{-1}$	*Kirkby et al., 2004*
Evapo-transpiration intensity	*ET*	$mm.y^{-1}$	*Pistocchi et al., 2006*
Area fraction of pasture soil	*FRP*	-	*PELCOM, 2005*
Area fraction of cropland soil	*FRC*	-	*PELCOM, 2005*
Area fraction of natural soil	*FRN*	-	*PELCOM, 2005*
Area fraction of surface water	*FRW*	-	*Pistocchi and Pennington, 2006*
Atmospheric mixing height	*H*	*m*	*Roemer et al., 2005*
Soil organic carbon content	*OCTOP*	-	*Jones et al., 2004*
OH-concentration in air	*OH*	$molec.cm^{-3}$	*Roemer et al., 2005*
*Precipitation intensity**	*R*	$mm.y^{-1}$	*Pistocchi et al., 2006; New et al., 2002*
Soil moisture content	*SM*	-	*Pistocchi et al., 2006*
Runoff from soil	*Q*	$mm.y^{-1}$	*Pistocchi et al., 2006*
Suspended matter concentration in water	*SPM*	$mg.l^{-1}$	*Pistocchi et al., 2006*
Atmospheric temperature	*T*	°C	*New et al., 2002*
Wind velocity at 10m	*U10*	$m.s^{-1}$	*New et al., 2002*
Aerosol deposition velocity	*AER*	$m.s^{-1}$	*Pistocchi et al., 2006*
Leaf area index	*LAI*	$m^2.m^{-2}$	*Pistocchi et al., 2006; MARS, 2005*
*Aerosol surface***	*Aersurf*	$m^2.m^{-3}$	*EMEP, 2006*
Water inflow in cell	*Inflow*	$m^3.s^{-1}$	*Pistocchi and Pennington, 2006*

Table 12: Environmental parameters taken into account in the calculations.
** A conversion was made from rainfall and snowfall intensity data to one value for precipitation. For this parameter, 10 mm of snowfall was set equivalent to 1 mm of rain.** The aerosol surface was estimated from PM10-concentrations. The average European PM10-concentration was set equal to the average aerosol surface default in BasinBox (1.5*10-4 $m^2.m^{-3}$; Brandes et al., 1996) and the aerosol surfaces in the different grid cells were made proportional to that.*

GIS-based model MAPPE (Pistocchi and Pennington, 2006), and were collected from continental and global scale data sets available from different sources (Pistocchi and Pennington, 2006; Pistocchi et al., 2006). Details about individual parameters were discussed in (Pistocchi et al., 2006).

Maps of Europe with single environmental properties were rasterized into grid cells within which the environmental property values were averaged. An overlay

was made of all raster maps with individual parameter values. From this overlay, a property-combination table was created, containing all environmental properties for each grid cell, and environmental concentrations were calculated for each cell with its own characteristic set of environmental properties. For some parameters, the values were unknown for one or more cells. In those cases, the average parameter value of the other cells was applied. If more than one third of the parameter values for a given cell was unknown, this cell was not taken into account in further calculations. This was the case for 15% of the 250x250 km cells. With the exclusion of these cells, 137 unique environmental property combinations were derived for the European continent (see Appendix E3). Calculations were performed for a group of 200 organic chemicals taken from Huijbregts et al. (2005), showing a wide range in chemical partitioning properties and half-lives. The physical-chemical properties of the chemicals used in this study are given in Appendix E1.

Concentration ranges

Environmental concentrations were predicted in three compartments: air, water and soil. For each scenario, concentration ranges (CR) between the different compounds, defined as the ratio between the 95^{th} and 5^{th} concentration percentiles, were calculated for each regional cell separately. The concentration ranges between the cells were obtained for each individual compound. Additionally, the concentration range of the total set of concentrations was calculated per scenario (CR_{total}). From this, the average concentration ranges caused by compound differences ($CR_{chemical}$) and the average concentration ranges caused by environmental differences (CR_{area}) were derived. The variation in concentration ranges, represented by the 95-percentile level of the CRs (95% CR-levels), were also calculated. For each scenario, the CRs were plotted to show the relative influence of respectively compound variability and environmental variability on the total variation in environmental concentrations.

Stepwise multiple regression

The contribution of each of the individual input parameters to the total concentration range was determined using stepwise multiple regression analysis (Darlington, 1990). Stepwise multiple regression is a way of computing OLS regression in stages. In each stage, the independent parameter that is best correlated with the dependent parameter is iteratively included in the equation. This process is repeated until the addition of a remaining independent parameter does not increase R^2 by a significant amount. The R^2-values derived from the model equations indicate the relative influence of each of the individual parameters on the total concentration variation, which was the dependent parameter in this study. For the purpose of this study, $p = 0.05$ was chosen as the significance limit for parameters to be entered in the model equation. The 20 environmental parameters were taken into account as predictor variables, as well as the main physical-chemical properties: air-water and soil-water partitioning coefficients (K_h resp. K_p), and the degradation rate constants in air, water and soil. Parameters with a skewed distribution were log-transformed and fractions were transformed to $-\infty$ to $+\infty$ in order to meet the demand for normally distributed variables. Furthermore, mutually correlated parameters were

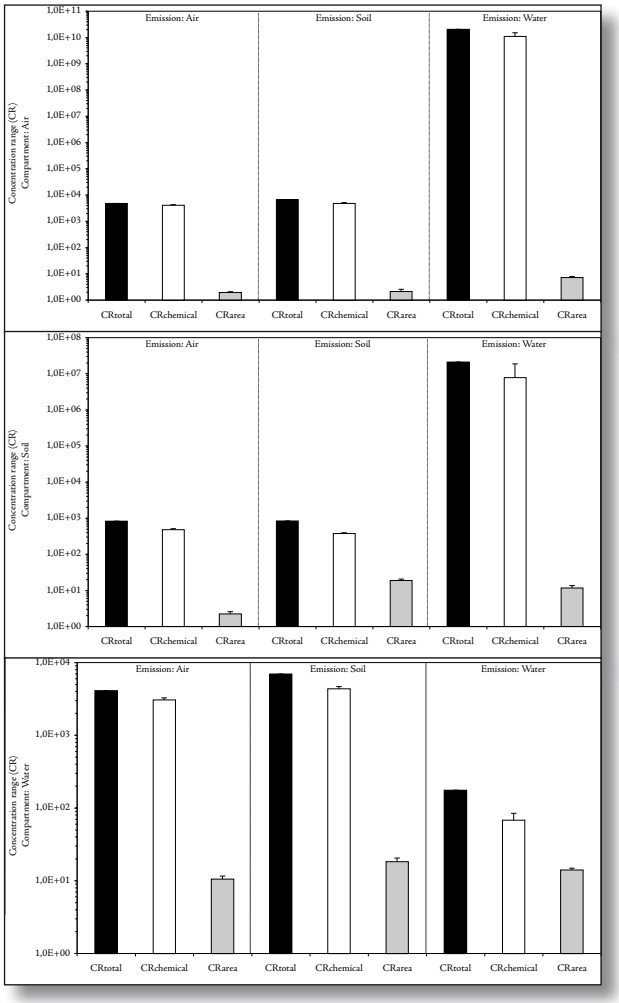

Figure 26: The average concentration ranges (CR) for the environmental concentrations in Europe, for three different emission scenarios. Concentration ranges are given for the total concentration variation (CR_{total}; black bars), the concentration variation caused by the variation in substance properties ($CR_{chemical}$; white bars) and the concentration variation caused by differences in environmental characteristics (CR_{area}; gray bars). 26a: Concentration ranges in the air compartment, 26b: Concentration ranges in the soil compartment, 26c: Concentration ranges in the water compartment. The error bars indicate the 95% CR-levels.

excluded from the analysis ($R^2 > 0.6$). This was the case for eight of the environmental parameters and for the degradation rate constants in soil and water (see Appendix E4). The degradation rate constant in water ($K_{degwater}$) was renamed to '$K_{degw/s}$' due to the almost 1:1 correlation between $K_{degwater}$ and $K_{degsoil}$.

Results

Concentration ranges. In Figure 26a, the predicted concentration ranges in the air compartment are given. Figure 26a shows that the CR_{total} ranges from about 3 to 9 orders of magnitude, being smallest if emissions occur to air or soil, and largest if emissions occur to water. In all scenarios, the CR_{total} is mainly caused by the variation in substance properties; $CR_{chemical}$ is always at least 3 orders of magnitude larger than CR_{area}. Figure 26b shows the concentration ranges in the soil compartment. Here, it can be seen that the CR_{total} ranges from about 3 to 7 orders of magnitude, being smallest if emissions occur towards soil or air, and largest if emissions occur to water. $CR_{chemical}$ always dominates the CR_{total}. The $CR_{chemical}$ is about a factor 200 larger than the CR_{area} if emissions take place to air, and five orders of magnitude larger if emissions take place to water. For soil emissions, the ratio $CR_{chemical}/CR_{area}$ is only a factor 20. In Figure 26c, the concentration ranges in the water compartment are given. It shows that the CR_{total} ranges from about

2 to 4 orders of magnitude in the water compartment, being smallest if emissions occur to water and largest if emissions occur to soil. If emissions take place to air or soil, the $CR_{chemical}$ is about 150 times larger than the CR_{area}. In case of emissions to water, the CR_{area} is relatively large compared to $CR_{chemical}$. In this scenario, the ratio between $CR_{chemical}$ and CR_{area} is a factor 5.

Stepwise multiple regression

Figure 27 shows the R^2-values obtained from the stepwise multiple regression analyses. The three most relevant parameters are given, with the corresponding R^2 of the regression equations, as well as the R^2 of the final regression model in which all significant parameters ($p<0.05$) were taken into account. The final regression models of all scenarios have a R^2 larger than 0.65, except the soil scenarios with emission to air ($R^2=0.41$) or soil ($R^2=0.51$). It can be observed that in all scenarios, one or more of the physical-chemical properties (white bars) explain the largest part of the concentration variation.

For air concentrations caused by emissions to air, the R^2 is dominated for more than 99% by the air-water partition coefficient (K_h). If emissions occur to soil, K_h also largely determines R^2, followed by the degradation rates in soil and the rain intensity. If emissions occur to water, the degradation rates in water, as well as the water depth are the most explanatory variables. For soil concentrations, the partition coefficients between soil-water (K_p) and air-water (K_h), and the degradation rates in soil belong to the most influential parameters, whereas the environmental characteristics temperature and the fractions of agricultural soil and surface water play a role in respectively the emission scenario to soil and to water.

The variation in water concentrations is also largely determined by the chemical properties K_p, K_h and the degradation rates in water. If emissions occur to water, the fraction of surface water belongs to the three most explanatory variables as well.

Discussion

Environmental concentration variations

The results of this study show the relative influence of substance properties and of environmental characteristics on the variation in environmental concentrations of chemicals for different scenarios in Europe. In the present study, emissions were set to take place to the nested cell, and regional environmental concentrations were considered only. The influence of the regional emissions on the area outside the region, and the influence of continental or global emissions on the regional scale cell have not been studied. Furthermore, unit emissions were assumed.

In most multimedia fate models, it is assumed that chemical properties primarily account for the variation in environmental concentrations. This assumption was already nuanced by Webster et al. (2004), who concluded that the quality of results obtained from regional environmental fate models can be improved by the use of region-specific landscape parameters. Hertwich et al. (1999) performed a sensitivity study on the variance in the potential dose to physical-chemical properties, exposure parameters, and environmental

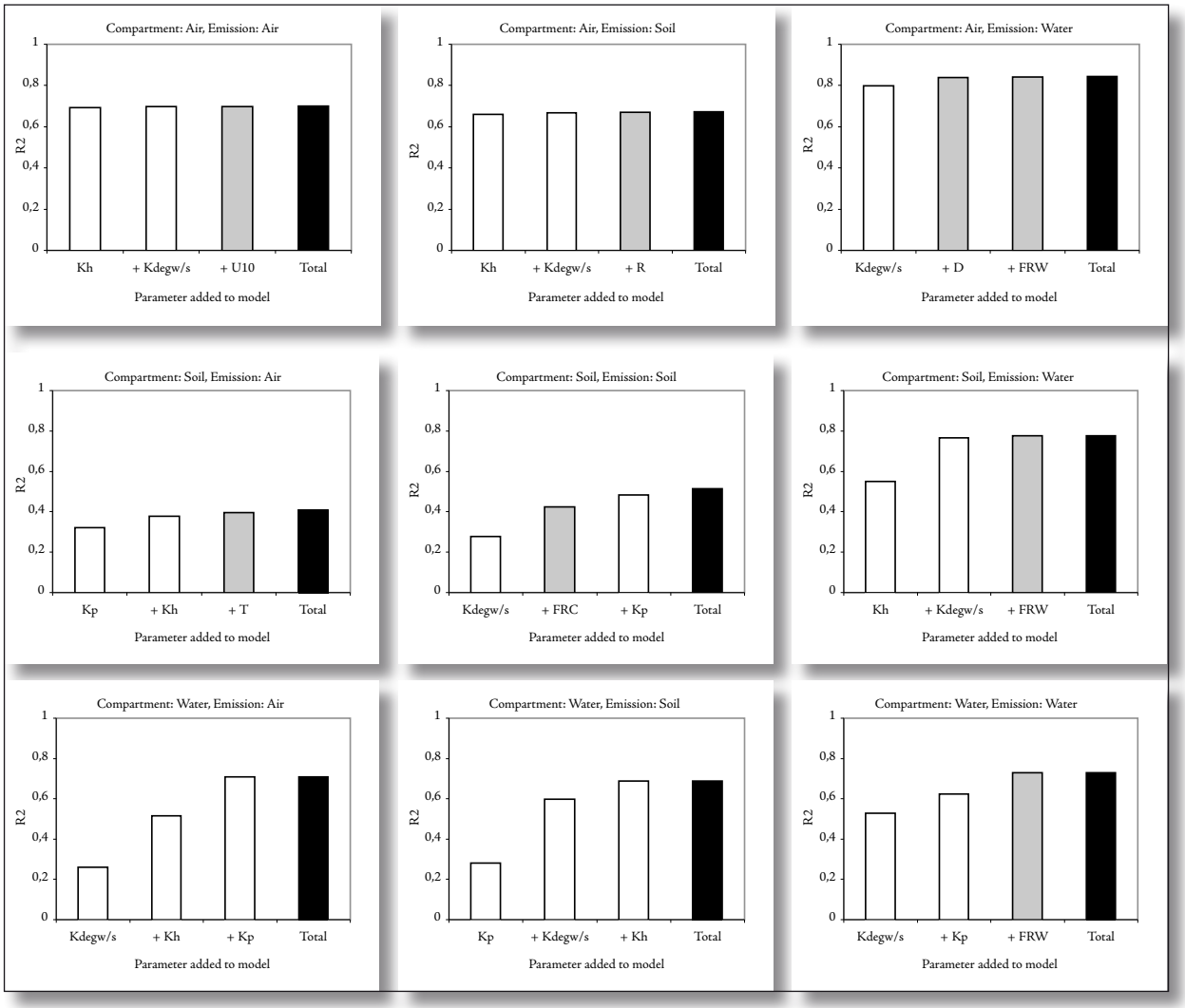

Figure 27: R^2-values of the regression equations obtained from the stepwise multiple regression analyses. The three most relevant parameters (chemical properties in white bars and environmental characteristics in gray bars) are given, with the corresponding R^2 of the regression equations, as well as the R^2 of the final regression model (black bars) in which all significant parameters ($p<0.05$) were taken into account. K_h = air-water partition coefficient, $K_{degw/s}$ = degradation rate in water/soil, U10 = wind speed, R = rain intensity, D = water depth, FRW = fraction surface water, T = temperature, FRC = fraction agricultural soil, K_p = soil-water partition coefficient.

input parameters. From that study it was concluded that for most compounds, physical-chemical properties or exposure parameters largely account for the concentration variance. Consistently with the findings of Hertwich et al. (1999), Fenner et al. (2005) concluded that the ranking of chemicals based on their overall persistency (P_{ov}) and long range transport potential (LRTP) is largely determined by the chemical properties. For compounds that are mainly present in the air compartment, our results are most similar to those of Hertwich et al. (1999). For compounds that reside in the soil and water compartments, chemical properties still account for the largest part of the concentration variation, although the present study shows that environmental parameters can play a role in the total concentration range as well.

In general, except for the air compartment, the average concentration range caused by the variation in environmental characteristics (CR_{area}) is always larger in the compartments to which the emission occurs. This can be explained by the fact that transport processes from the emission compartment towards the other compartments are mainly driven by the physical-chemical properties of the compound, and therefore concentration differences in the secondary and tertiary compartments are mainly caused by substance differences. In case air is the primary compartment, the environmental characteristics are less influential due to the mobility of this medium and its rapid mixing.

Air concentrations

In all scenarios in which concentrations in air were considered, substance properties almost fully account for the variation in environmental concentrations. The air-water partition coefficient (K_h) is the main parameter causing the variation in predicted concentrations if emissions occur to air or soil. This parameter determines the amount of atmospheric deposition and (re)volatilization and in that way influences the variation in air concentrations. Predicted concentration ranges in the air are largest if emissions occur to water, due to large differences in the volatizing fractions of the different compounds, which is in this compartment mainly caused by different degradation rates in water. To a lesser extent parameters that determine the water residence time in the cell play a role (water depth and the fraction of surface water in a cell). The absolute concentrations in air in this scenario are low to extremely low, because generally a small fraction of the emitted substance leaves the water compartment.

Soil concentrations

In the soil compartment, environmental characteristics play a more important role in determining chemical fate with respect to substance properties than in the air compartment, particularly if emissions occur to soil. In this compartment, the variation in environmental characteristics such as the fractions of cropland soil and water, the organic carbon content of soils, and temperature influence the variation in soil concentrations. However, the degradation rates and the partitioning coefficients are the most influential parameters on the concentration variations. K_p and K_h respectively determine the amount of chemical loss from soil to water and air, and due to their large range between compounds as well as their significance in the modeled processes, they mainly determine the concen-

tration variation. The main environmental parameter is the fraction agricultural soil, determining the area to which emissions occur in a cell. It is obvious that between regions with small and large fractions of agricultural soils, different amounts of compounds are added to the system, resulting in different concentrations. Total concentration ranges in the soil compartment are largest if emissions occur to water. In that scenario, transport processes between air, water and soil plays a role, since the only transport route of chemicals from water to soil is via the air. This means that the majority of the physical-chemical properties and environmental characteristics are involved in the fate calculations, resulting in a wide spread of predicted concentrations.

Another finding for the soil compartment is that the 95% CR-levels are relatively high for the CRarea in the water emission scenario: for a small number of compounds, the concentration variation in the soil between the different regional cells is relatively large. This is the case for those chemicals for which volatilization and deposition are relatively important transport processes. The spatial variation in deposition is large, for example, for chemicals with a low Henry's law constant, due to differences in precipitation intensity throughout Europe. These outcomes are in accordance with those of Hertwich and McKone (2001), who found that the characteristic travel distance of these chemicals is predicted substantially different in model situations with and without rain. One should take into account that continuous rain is assumed in our level III model study, which may cause an overestimation of the substance removal from the atmosphere through wet deposition (Jolliet and Hauschild, 2005).

The R^2-values derived from the regression analyses indicate a rather high explanatory power ($R^2 > 0.65$) of the regression equations, except in the soil compartment. Although all possibly relevant parameters were taken into account, it appears that a linear regression equation is not capable for fitting environmental soil concentrations with a high explained variance.

Water concentrations

In the water compartment, the same chemical properties as in the soil compartment dictate the concentration variation. However, CR_{area} is relatively large in this compartment, with the largest relative influence of the environmental characteristics in the water emission scenario. In this scenario, a large fraction of the emitted substance stays in the water compartment, which means that at unit emissions, relatively small differences in concentrations appear between different compounds.

On the contrary, the area fraction of surface water substantially influences the variation in environmental concentrations, since it accounts for the residence time of water in a cell. These results, indicating that differences in water body characteristics may have a substantial impact on the water concentrations, are in line with Newham et al. (2003) and Pennington et al. (2005), who argued that when predicting concentrations with a non-spatial multimedia fate model, it is necessary to take into account spatial differences in residence times in the water compartment, such as large lakes. If emissions occur to soil, the main transport route of chemicals to water is by runoff. In this process, K_p is important, but also other substance

properties and environmental characteristics (rain intensities, soil organic carbon contents) are of influence, resulting in relatively large concentration ranges.

Model study setup

Our study refers to the variability in chemical and environmental properties. It has been shown, however, that the influence of the spatial distribution and the absolute intensity of emissions can dominate the concentration variations (Pennington et al., 2005; Sweetman et al., 2002). Besides, a dataset with European environmental characteristics was used for this study. The results of this study therefore apply to Europe, but it is expected that the outcomes will be the similar for other parts of the globe with comparable environmental conditions. However, in different environmental zones, particularly those with more extreme environmental conditions, the influence of the variation in environmental characteristics on the concentrations of substances may be quite different.

The calculations in this study were performed for cells on a 250x250 km scale. However, on a different model scale, other concentration ranges may occur. To check the possible influence of scale on the concentrations, we repeated the calculations on two smaller cell sizes: 100x100 km and 50x50 km. The outcomes of these calculations are given in the Appendix E5. In general, concentration differences in water and soil are predicted to be larger if a smaller regional cell is applied in the model calculations, and the relative influence of environmental characteristics on the total variation increases on a more detailed spatial scale. The concentration variations (CR_{total}) predicted on a 50x50 km scale can be up to a factor 5 larger than the spatial variations on a 250x250 km scale, whereas the concentration variations caused by environmental conditions (CR_{area}) can be larger up to a factor 10. For the air concentrations, however, the predicted total concentration variation decreases between the 250x250 km and 50x50 km scales. Also in this compartment, the CR_{area} increases with increasing model resolution, but the $CR_{chemical}$ becomes lower. Obviously, at a more detailed resolution, less variation between compounds is being modeled. The cause of this is that on a more detailed scale, the advection process becomes more important, and the inter-substance variation in advection is relatively small. Hertwich and McKone (2001) did not find any effect of (pollutant-specific) spatial scales on the potential concentration of chemicals. In contrast, other studies from related branches of environmental modeling show that the model scale significantly impacts the variability in model output (Zoras et al., 2007; Shrestha et al., 2006; Kavvas et al., 1998; Koren et al., 1999; De Wit et al., 2005; Oka and Hasumi, 2006). From our study, it can be concluded that for the air compartment, the differences in the spatial concentration variations are negligible between the 250x250 km and 50x50 km scales when unit emissions are assumed. In the soil and water compartments, the increase in spatial variation indicates that the choice of model scale can influence the predictions for single compounds in multimedia mass balance models up to a factor 10 between a 250x250 km and 50x50 km scale.

To identify the relative influence of each of the separate input parameters, a stepwise multiple linear regression was performed. In this regression procedure,

a linear relationship is assumed to exist between the predictor variable and the dependent variable (environmental concentration). In the reality of multimedia fate modeling, no such a linarity is expected. On the contrary, our models are designed to describe the complex, non-linear relationships which are expected to exist between concentrations in the environment on the one hand and substance properties and environmental characteristics on the other hand. However, in absence of other suitable methods, we have chosen to apply linear regression here merely to obtain a first indication of the relative importances of model parameters.

Implications for multimedia fate model studies

In this paper, we compared the relative influence of environmental characteristics with substance properties on the concentration variations of substances in Europe. The results of this study provide information for which emission-receiving compartment scenarios, incorporating spatial differences in environmental parameters can be important. Depending on emission scenario and compartment, the range in predicted environmental concentrations spreads from 2 up to 9 orders of magnitude. Our study supports the assumption that the variation in the fate of chemicals in the environment is, beside emission intensity, mainly dependent on substance properties. This means that for many regulatory purposes, the current use of well-mixed multimedia fate models, in which chemical-to-chemical differences in model outcomes are met, while the environmental characteristics are disregarded by limiting the analyses to modeling 'typical' or 'average' conditions only, does give suitable results. From our study it however appears that, particularly regarding the influence of direct emissions on soil and water concentrations, environmental differences should not be ignored when estimating concentrations.

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8 General discussion

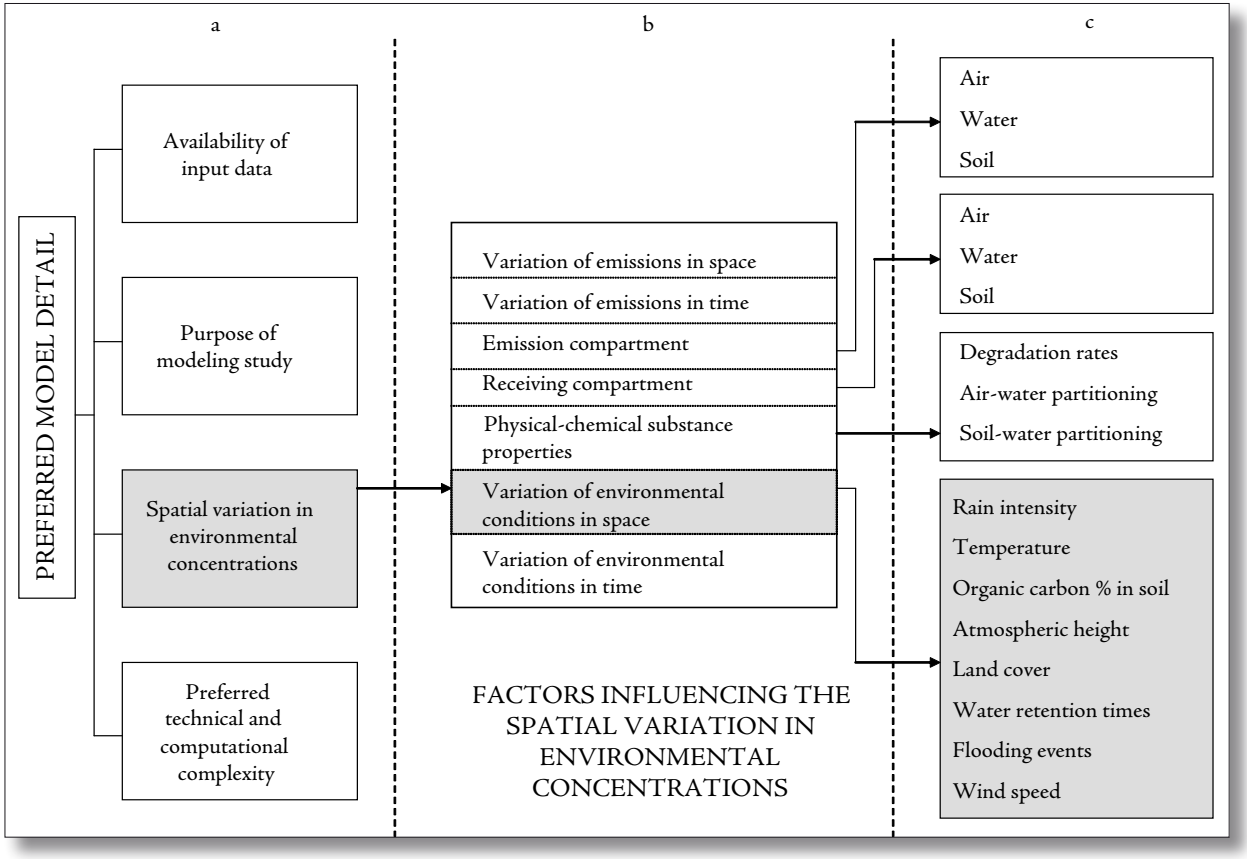

Figure 28: Schematic overview of the factors influencing the preferred multimedia mass balance model detail, which forms the general framework of this thesis. 28a (left): The main criteria determining the preferred model detail. 28b (middle): Factors influencing the spatial variation in environmental concentrations. 28c (right): Examples of factors mentioned in 28b.

The optimal model detail in a chemical fate study should follow from the purpose of the study (Figure 28a). When determining the purpose of a modeling study, the preferred precision of the model outcomes needs to be chosen. And to achieve that precision, the preferred spatial detail in model outcomes has to be defined. The model detail that is required to achieve the desired spatial detail in model outcomes is partly dependent on the (expected) spatial variation in environmental concentrations in reality, a topic

that formed the general framework of this thesis. The main goal of this thesis was to analyze the relative importance of the spatial variability in environmental conditions on the spatial variation in environmental concentrations. To this end, the aim was to indicate which factors influence the spatial variation in environmental concentrations, to which extent they are of importance, and how they are related to the factor 'spatial variability in environmental conditions'.

The factors determining the spatial variation in environmental concentrations are summarized in Figure 28b. The three main categories are the emissions (their variation in space and in time, the emission compartment), the physical-chemical properties of the substance, and the environmental conditions (their variation in space and in time, the receiving compartment). Most of these factors have been subject of one or more of the studies presented in this thesis. In the current chapter, a comprehensive overview of the study outcomes regarding each of these factors is given. Further, it is analyzed how each of these factors relate to each other, and particularly to the factor 'spatial variation in environmental conditions'. Based on the insights obtained, the spatial variation in environmental concentrations can be explained and predicted, and thus, it will be easier to decide whether application of a spatially explicit model is required and which model resolution is desirable for a certain study, depending on the purpose of the study. Practical implications for the preferred spatial detail for some modeling purposes are formulated.

Explaining spatial variation in environmental concentrations

The influence of spatial variability in environmental conditions

Landscape and climate characteristics vary between different locations, laterally as well as vertically (Cowan et al., 1995, McKone and Bennett, 2003). A number of those environmental characteristics influence the behavior of chemicals in the environment, and resulting in variation of chemical concentrations in space. The relative importance of the spatial variability in environmental conditions on the spatial variation in environmental concentrations calculated with multimedia mass balance models formed the central issue in this thesis. In Chapter 2, the fraction organic carbon (as confirmed by Hertwich et al., 1999), the depth levels of the drainage and the surface run-off intensity were identified as crucial factors for the vertical concentration profile of chemicals in soils. In Chapter 3, the intensity of tillage activities, bioturbation and cryoturbation were added as important influences in this context (Cousins et al., 1999; McLachlan et al., 2002). In Chapter 4, it was concluded that water-based transport of chemicals, which occurs in downward direction of the river basin, as well as the presence/absence of periodically flooded areas cause variation in chemical concentrations between the upstream and downstream areas. In Chapter 5, PCB-153 concentrations predicted by the LOTOS-EUROS model, in which four atmospheric layers are present, and by SimpleBox, having one air compartment, were compared. Due to the layered structure of the atmosphere in LOTOS-EUROS, this model accounts for differ-

ences in vertical air characteristics, influencing the chemical transport from air to soil and vice versa. This model feature leads to different concentration predictions than those of SimpleBox, indicating the relevance of vertical spatial differences in air characteristics and resulting concentrations. The effects of vertically variable air conditions were also shown by Hertwich and McKone (2001).

From Chapter 7, it was concluded that, when considering concentrations of different chemicals at different locations, physical-chemical properties of substances largely determine the concentration variations. However, for single compounds, the spatial variation in environmental characteristics in Europe can result in spatial concentration variations up to two orders of magnitude. The environmental parameters that play the most important role appear to be the spatial variation in water retention times (as confirmed by Pennington et al., 2005), wind speed, and rain intensity for compounds in the air compartment. In the soil compartment, also the temperature and organic carbon content play a role, whereas in the water compartment, the water retention parameters are the main determining environmental parameters.

Environmental conditions thus partly determine the environmental fate of substances, and from the studies presented in this thesis, it can be concluded that this influence may be significant. The spatial variation in environmental conditions may cause spatial concentration differences up to a few orders of magnitude; the systematic study performed in Chapter 7 shows a lateral variation of two orders of magnitude for the European situation. Also from other studies, the influence of spatially varying environmental conditions on the spatial variation in environmental concentrations has come forth. For example, Webster et al. (2004) showed that differences in the rain rate, water and air residence times, relative surface water area and temperature can cause differences in residence times of chemicals up to 65% in different regions of Canada. The variance in environmental chemical concentrations due to uncertainty and variability in landscape parameters has further been examined for different regions, e.g. the California region (Hertwich et al., 1999; McKone, 1993), southern Ontario (MacLeod et al., 2002), and regions of Europe (Berding and Matthies, 2002). Also in these studies, the general tendency was that the spatial variation in environmental conditions can be a significant factor in determining concentration variations, up to more than one order of magnitude. However, the uncertainty and variability in environmental conditions are generally subordinate to the uncertainty and variability in substance data and emissions. Beside lateral concentration differences, it was shown in this thesis and other studies (Chapters 2, 3 and 5; Hertwich and McKone, 2001) that significant vertical concentration variations may be caused by the vertical spatial variation in environmental conditions. Also time-varying environmental conditions can have an impact on the spatial concentration pattern of chemicals, which is for example shown by intermittent rain events that enlarge/reduce certain chemical process intensities (Hertwich et al., 1999; Jolliet and Hauschield, 2005). However, this time-factor was hardly taken into account in this thesis, and therefore will not be considered further here.

Receiving compartment. The effect of the spatial variation in environmental conditions on the chemical concentrations is different for the environmental compartments. The outcomes of Chapter 7 indicate that in the different receiving compartments significantly different environmental concentration ranges are present at equal emission intensities. Depending on the emission scenario, the spatial concentration variations present in the air, water and soil compartments differ up to two orders of magnitude, whereby the greatest spatial concentration variations are found in the soil and water compartments. This means that the spatial differences in environmental conditions have the greatest effect on the concentration variation in these compartments.

Also from the other studies, differences in spatial concentration variations between the environmental receiving compartments are found. Modeling concentration ratios between the upstream and downstream areas of the Rhine with emissions to soil or water results in large concentration variations in the cropland soil and river water compartments, whereas concentrations in the air compartment are relatively homogeneously distributed over the whole river basin area in both emission scenarios. Chapter 5 calculates spatial ranges in concentrations of PCB-153 in air and soil. Also in this scenario, spatial air concentration ranges are smaller than the soil concentration ranges, which is also reflected in the range of measured concentrations throughout Europe. These outcomes provide a general indication that the spatial variability in environmental concentrations is greater in the soil and water compartments than in the air compartment.

The studies presented in this thesis further showed that the relative importance of the spatial variability in environmental concentrations can be strongly dependent on some of the other factors given in Figure 28. The compartment to which the chemical substances are released strongly determines the spatial variation in environmental concentration variations. The same is the case for the substances under consideration. The way these factors relate to the spatial variation in environmental conditions, will be elaborated in the next section.

Other factors influencing the spatial variation in environmental concentrations

Emissions

Emission intensities. Emissions of chemical substances can originate from diffuse sources as well as from (multiple) point sources. Several literature sources report on the importance of the spatial variation in emission intensities, which can amount to several orders of magnitude, on the spatial variation in environmental concentrations. Although often highly uncertain, it has been shown that the influence of the spatial distribution and the absolute intensity of the emissions can dominate the concentration variations over all other parameters (Bennett et al., 1999; Sweetman et al., 2002; Pennington et al., 2005). This thesis confirms that the spatial variability in emission intensities can be the most determining factor in spatial concentration variations. In Chapter 4, the trend of increasing chemical concentrations in the downstream direction of the river Rhine basin predicted by Bas-

inBox is mainly attributed to differences in emission intensities due to low upstream population density and agricultural activities. Concentration patterns of PCB-153 in air and soil, predicted by LOTOS-EUROS and SimpleBox in Chapter 5, largely reflect the spatial emission pattern of this compound. For example, the range in the soil concentration pattern of three orders of magnitude on the example map of 1985 is almost fully accounted for by the range in spatial emission intensities. Moreover, in Chapter 6 it was observed that the difference in predictions of chemical export flows between spatial and non-spatial models is large in model scenarios with a heterogeneous spatial emission pattern. This could be explained by the fact that chemical concentrations in such a scenario differ from the average concentrations in the edge-cells of models, resulting in differences in chemical concentrations.

The results presented here confirm the general idea that the spatial variation in emission intensities, which are directly proportional to the concentrations, is a crucial factor in determining the spatial variation in environmental concentrations. It can be concluded that if the emission intensities of a compound are highly heterogeneous within the study area, and the influence of this heterogeneity is to be evaluated by the model, a spatially explicit model has to be used to determine the environmental concentrations.

Variation of emission intensities in time, even on a fixed location or in a fixed area, can influence the spatial concentration patterns too, since these dynamic emissions result in variable transport flow directions and –intensities, lateral as well as vertical. However, this factor is hardly accounted for in this thesis, and therefore will not be considered further here.

Emission compartment. Chemicals are generally emitted towards the air, water or soil compartment. The way chemicals enter the environment influences their further environmental behavior (Mackay et al., 1996; Cahill and Mackay, 2003; Webster et al., 2004). In this thesis, several studies have been performed in which different modes of entry of chemicals into the environment were modeled. Chapter 7 calculates the environmental concentrations of 200 organic chemicals after emissions towards air, water or soil. The outcomes of this study indicate that between the different emission compartments, at equal emission intensities, the environmental concentrations ranges differ up to several orders of magnitude. If concentrations in air or soil are considered, emissions towards water yield concentration ranges that are much larger than if emissions occur towards air or soil; the differences in the concentration ranges mount up to six orders of magnitude between the different emission scenarios. If looking at water concentrations, emissions to soil result in the largest predicted concentration ranges, being two orders of magnitude larger than if emissions occur to water. This means that spatial differences in environmental conditions have the largest effect on the concentration variation if these emission compartments are concerned. In Chapter 4, similar results were found. In the case study for the river Rhine basin area, predicted concentration differences between the upstream and downstream areas are larger, and for more compounds, if emissions occur to water or soil than if emissions occur to air. Due to the rapid mixing

of chemicals after emission to the atmosphere and because air-based chemical transport takes place both in upstream and in downstream directions, the concentration differences between the downstream area and the upstream area remain relatively low. The outcomes of Chapters 4 and 7 provide a general indication that the spatial variability in environmental concentrations is larger if emissions occur to water or to soil (as confirmed by Cahill and Mackay, 2003), than if emissions occur to air, due to the relatively rapid mixing within the air compartment. However, the influence of emission compartment on the spatial concentration variation is strongly related to the receiving compartment that is considered and to the physical-chemical properties of the compound. If the air is the receiving compartment, and heterogeneous emissions occur also to air, as indicated in Chapter 6, the spatial variation in concentrations may be very significant. Also, in Chapter 7, highly variable air concentrations between chemical substances are predicted in the case if emissions occur to water, due to large differences in the air-water partition coefficient of the different substances. This means that a large variation exists between substances in the amount of chemical that will diffuse from the water towards the air compartment.

Physical-chemical substance properties

The third main factor in determining the spatial variation in environmental concentration is the physical-chemical character of the substance(s) under consideration. The way a chemical substance behaves in the environment strongly depends on its physical-chemical characteristics that determine the partition behavior between environmental media, as well as its degradability (Hertwich et al., 1999; Huijbregts et al., 2000; Mackay, 2001). Also, these chemical properties influence the tendency of a chemical whether or not to show a wide variation in environmental concentrations within the different environmental compartments. In this thesis, this factor has come up front in several sections, of which Chapter 7 gives a general overview on the influence of physical-chemical properties on the variation in predicted environmental concentrations. It shows that the predicted environmental concentration range between 200 different chemicals can mount up to nine orders of magnitude due to different physical-chemical properties only. That study concludes that when chemicals are evaluated with different properties, the influence of the properties plays a more important role in the total concentration variation than the environmental characteristics do. This is confirmed by the model comparison study of Chapter 6. In this chapter, P_{ov} and LRTP estimates for 14 chemicals were similar for the different models with different characteristics, due to the relatively large influence of the physical-chemical properties of the modeled compounds.

Although Chapter 7 perfectly indicates the importance of substance properties on the fate of chemicals, it does however not treat the issue of the influence of physical-chemical properties on the variation in concentrations in space. This issue is firstly discussed in Chapter 2 for the soil compartment. In this chapter, the predicted soil concentration profiles for eight different chemicals were compared, showing that the magnitude of the concentration decline in soil with depth strongly varies between the different compounds. In the example

calculations, the greatest effect of the model adaptations was observed for substances with the smallest penetration depth, which are the readily degradable and relatively immobile substances.

In Chapter 4, 3175 hypothetical chemicals were taken into account in the estimation of concentration ratios between an upstream and downstream river basin area. For a number of compounds, the concentration ratio appears to be larger than a factor of 100, while for other compounds hardly any differences can be found between upstream and downstream concentrations. From Chapter 7, the properties that influence the spatial concentration variation most turn out to be the air-water (K_h) and soil-water partition coefficient (K_{sw}) and the degradation rate constants in soil and water, which is confirmed by the outcomes of the studies in Chapters 4 and 6. This means that the distribution of chemicals between the environmental compartments is largely dependent on their partitioning behavior, rather than on certain advective processes.

It appears that spatial differences in environmental conditions have the largest effect on the concentration variation if substances are concerned with a relatively low K_h and/or high K_{ow}, which tend to mainly reside in the soil and water compartments, and/or low degradation rate constants. It can be concluded that for different chemicals significant differences exist in the spatial variation in environmental concentrations. Environmental concentration ranges within an area can vary between different substances up to several orders of magnitude.

Practical implications: selecting the appropriate model for a modeling study

Since not all factors indicated above and in Figure 28 were studied quantitatively, and since many relationships exist between the different factors, it is difficult to state which factor is the most important in determining the spatial variation in environmental concentrations. However, from the modeling studies presented in this thesis, it is possible to indicate qualitatively which factors are relatively important in most cases and which are not. The spatial variation in emission intensities was identified as the most influential parameter on the spatial variation in concentrations. The range in emissions is directly proportional to the concentrations and can mount up to several orders of magnitude, so it can easily overrule all other spatial factors. However, one should take into account that in case of diffuse, homogenously distributed emissions, this factor can sometimes be neglected. Also the physical-chemical properties, particularly K_h, K_{ow} and the degradation rate constants, of the substance under consideration play an important role, not only for its general environmental fate, but also for the spatial variation that occurs in environmental concentrations. For assessments including multiple chemicals, it is obvious that this factor should not be neglected. The spatial variation in environmental conditions can also play a significant role, depending on the actual environmental conditions variability, and particularly in scenarios with emissions to water or soil, for compounds with a relatively low K_h and/or high K_{ow}, and if the water or soil compartment is considered. The factor of spatial environmental condition variation be-

1) What is the multimedia fate modeling purpose?			
	Location-specific		*> Question 2*
	Abstract (i.e. P_{ov} estimations)		*> Generic box model*
2) What is the preferred precision of the model outcomes?			
	High		*> Question 3*
	Low		*> Generic box model*
3) What is the spatial variation in emission intensities?			
	Unknown		
		Probably one point source/distributed point sources	*> Site specific (nested) box model*
		Probably overlapping point sources	*> Question 4*
		Probably homogeneous	*> Question 4*
	Known		
		One point source/distributed point sources	*> Site specific (nested) box model*
		Overlapping point sources	*> Spatially explicit model*
		Homogeneous	*> Question 4*
4) Is the compound under consideration accessible to vary in space (low K_h, high K_{ow}, low degradability)?			
	Yes		*> Question 5*
	No		*> Site specific box model*
5) What is the spatial variation in environmental conditions (mainly water retention time, rain intensity, OC% in soil)?			
	Unknown		*> Generic box model*
	Known	*Homogeneous*	*> Site specific box model*
		Heterogeneous	*> Question 6*
6) What is the emission compartment?			
	Air		*> Question 7*
	Soil/Water		*> Spatially explicit model*
7) What is the receiving compartment?			
	Air		*> Site specific box model*
	Soil/Water		*> Spatially explicit model*

Figure 29: Decision scheme for determining the preferred multimedia fate model type, based on the purpose of the modeling study, the preferred precision of the model outcomes, spatial variation in emission intensities, physical-chemical substance properties, spatial variation in environmental conditions, source and receptor compartments. Generic box models, site specific (nested) box models and spatially explicit box models are distinguished.

comes relatively important if emissions are distributed more homogeneously over the study area.

Further research can focus on a quantitative priority setting of the different factors influencing the spatial variation in chemical concentrations under different circumstances, and for different modeling purposes. However, based on the results derived from this thesis, general guidelines can be formulated, indicating when to use a spatial model and when to use a non-spatial model, either a generic or (nested) site specific model. In general, the principle of Parsimonius applies: 'as simple as possible, but as complex as necessary'. A schematic representation of these guidelines is given in a decision scheme in Figure 29. As indicated in this figure, the purpose of the modeling study and the preferred precision of the model outcomes are the first criteria whether or not to choose for a spatially explicit model in a specific study. The other criteria are respectively the availability of spatially explicit emission data, the spatial variation in emission intensities, the nature of the substance(s) under consideration, the spatial variation in environmental conditions, the emission compartment and the receiving compartment.

A few main modeling purposes are worked out following this decision scheme:

1) Regional risk assessments of single chemical substances to protect certain locations or groups of organisms (preferred precision is high): The spatial variation in emission intensities can be a main factor in determining the spatial concentration variations of chemicals. Therefore, the spatial detail of the applied multimedia mass balance model should be in line with the spatial emission variation. The choice for a model resolution depends on whether a substance is emitted:
Homogeneously over the area or by multiple point sources equally distributed over the area: the spatial variation in concentrations due to emissions will be low. Only if detailed model outcomes within the study area are preferred, a spatially explicit model should be considered, since that does account for the spatial variation in environmental conditions. Whether or not to decide to use a spatially explicit model than depends on the substance(s) under consideration, the emission compartment and the receiving compartment(s).
By overlapping point sources, resulting in a heterogeneous emission pattern over space. Therefore, the use of a spatial model is preferred to assess concentration differences within the study area.
By a single point source: the emission intensity will show a smooth gradient over space, which can be simulated with a spatial model, but more easily with a non-spatial model.
Independent of the emission pattern, in general, entering spatially variable environmental characteristics in the model will yield more reliable concentration estimations, particularly when emissions occur to soil or

water, and/or the concentrations of concern are soil or water concentrations, and/or chemicals are concerned that have a relatively high K_{ow} or a low K_h, which tend to mainly reside in the soil or water compartment. Taking into account depth dependent soil concentrations will improve the model predictions, either with a 'standard' soil penetration depth of 10 cm, or, if information is available on the local soil conditions, with a site-specific penetration depth.

2) Screening assessments of multiple chemicals: If the relative risk of large numbers of chemicals has to be estimated, for example according to their overall persistence (P_{ov}) or long-range transport potential (LRTP), mainly the physical-chemical properties of the substances are of importance, since P_{ov} and LRTP are largely influenced by the partitioning properties and degradation rates of chemicals (Fenner et al., 2005). To a lesser degree, the spatial emission variation, the emission compartment and the spatial variation in environmental characteristics influence those risk indicators. However, for practical reasons, screening assessments of multiple chemicals should be preferably performed with non-spatial generic box models, which will usually yield reliable results. To achieve reliable results, it will not be necessary to take into account depth dependent soil concentrations.

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9 Appendices

Appendix A: Supporting information 'Validation of predicted exponential concentration profiles of chemicals in soils'

Appendix A1: **Locations, compound types and environmental characteristics of the measurements sites**

Appendix A2: **Chemical specific input data for SimpleBox**

Appendix A3: **Calculated d_p, c_0 and uncertainty factors between the measured and the predicted soil concentration profiles. Values are given for the fits with a fixed d_p (theoretical model), and for the fits without a fixed d_p (regression model)**

Appendix A4: **Tables of the measured data points and the calculated soil concentration profiles from the theoretical model of Equation 5**

Profile #	Country	Location	Soil type	Rain rate mm.y-1	Temperature °C	Soil org. C % OC.drysolid-1	Compounds	Reference
1-4	Sweden	Nyänget, Heden	Natural	472a	1.1a	n.a.	citrate, oxalate	Van Hees et al., 2005
5	Sweden	Hasslöv	Natural	719a	7.9a	n.a	oxalate	Van Hees et al., 2005
6-17	Germany	Hessisches Ried	Agricultural	678a	9.4a	n.a.	antracene, benzo(a)anthracene, benzo(k)fluoranthene, benzo(a)-pyrene, chrysene, fluoranthene, indeno(1,2,3-c,d) pyrene, dibenzo-(a,h)anthracene, benzo(g,h,i)pery-lene, perylene, phenanthrene, pyrene	Gocht et al., 2001
18-32	Germany	Bonn	Agricultural	543a	9.7a	3.7	acenaphtene, anthracene, benzo-(g,h,i)perylene, benzo(a) anthracene, benzo(b)fluoranthene, benzo(k)-fluroranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, chrysene, fluo-ranthene, fluorene, indeno-(1,2,3-c,d)pyrene, naphtalene, phenanthrene, pyrene	Atanassova and Brüm-mer, 2004
33-34	United Kingdom	Park Grass	Natural	717	9.2	3.4	total-PCB, total-PAH	Cousins et al., 1999
35-36	United Kingdom	Broadbalk	Natural	717	9.2	2.7	total-PCB, total-PAH	Cousins et al., 1999
37-38	United Kingdom	Glengsaugh	Natural	1056	7.3	11.1	total-PCB, total-PAH	Cousins et al., 1999
39-40	United Kingdom	Hartwood	Natural	1045	7.1	12.4	total-PCB, total-PAH	Cousins et al., 1999
41	France	Burgundy	Agricultural	736a	10.1a	1.9	diuron	Landry et al., 2005
42	France	Burgundy	Agricultural	736a	10.1a	1.2	diuron	Landry et al., 2005
43	France	Burgundy	Agricultural	736a	10.1a	1.3	oryzalin	Landry et al., 2005
44	France	Burgundy	Agricultural	736a	10.1a	2.0	diuron	Landry et al., 2005
45	France	Burgundy	Agricultural	736a	10.1a	2.1	oryzalin	Landry et al., 2005
46	France	Burgundy	Agricultural	736a	10.1a	2.8	diuron	Landry et al., 2005
47	France	Burgundy	Agricultural	736a	10.1a	2.2	oryzalin	Landry et al., 2005

Profile #	Country	Location	Soil type	Rain rate mm.y-1	Temperature °C	Soil org. C % OC.drysolid-1	Compounds	Reference
48	Slovakia	Ziar	Natural	827a	5.8a	11.6	total-PAH	Wilcke et al., 1996
49	Slovakia	Ziar	Natural	827a	5.8a	9.1	total-PAH	Wilcke et al., 1996
50	Slovakia	Ziar	Natural	827a	5.8a	12.8	total-PAH	Wilcke et al., 1996
51-58	Portugal	Sorraia Valley	Agricultural	754b	16.5a	1.4b	atrazine	Azevedo et al., 2000
59-60	Portugal	Sorraia Valley	Agricultural	754b	16.5a	1.2b	atrazine	Azevedo et al., 2000
61-63	Germany	Starnberg	Natural	739a	8.5a	n.a.	OCDD, OCDF, 2,3,7,8-TCDF	Rotard et al., 1994
64-66	Germany	Schauinsland	Agricultural	962a	8.2a	n.a.	OCDD, OCDF, 2,3,7,8-TCDF	Rotard et al., 1994
67-75	Denmark	Ejby	Natural	850a	7.9a	n.a.	phenanthrene, fluoranthene, pyrene, benzo(b)fluoranthene, benzo(k)-fluoranthene, benzo(a)pyrene, benzo-(e)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene	Vikelsøe et al., 2002
76-84	Denmark	Sundbylille	Agricultural	850a	7.9a	n.a.	phenanthrene, fluoranthene, pyrene, benzo(b)fluoranthene, benzo(k)-fluoranthene, benzo(a)pyrene, benzo-(e)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene	Vikelsøe et al., 2002

a : IRI/LDEO Climate Data Library, b = Von Werner, 2005, n.a. – not available

Appendix A1: Locations, compound types and environmental characteristics of the measurements sites.

Name	CAS #	Mol. weight g.mol-1	Tmelt °C	Pvap 25°C Pa	Sol 25°C mg.l-1
acenaphtene	83-32-9	1.54E+02a	9.62E+01a	3.07E-01a	3.80E+00a
anthracene	120-12-7	1.78E+02a	2.16E+02a	1.00E-03a	4.50E-02a
atrazine	1912-24-9	2.16E+02a	1.74E+02a	4.00E-05a	3.00E+01a
benzo(a)anthracene	56-55-3	2.28E+02a	1.60E+02a	2.80E-05a	1.10E-02a
benzo(a)pyrene	50-32-8	2.52E+02a	1.75E+02a	7.00E-07a	3.80E-03a
benzo(b)fluoranthene	205-99-2	2.52E+02a	1.68E+02a	5.00E-07a	1.50E-03a
benzo(e)pyrene	192-97-2	2.52E+02a	1.78E+02a	7.40E-07a	4.00E-03a
benzo(g,h,i)perylene	191-24-2	2.68E+02a	2.77E+02a	2.25E-05a	2.60E-04a
benzo(k)fluoranthene	207-08-9	2.52E+02a	2.17E+02a	4.12E-06a	8.00E-04a
chrysene	218-01-9	2.28E+02a	2.55E+02a	5.70E-07a	1.60E-03a
citrate	77-92-9	1.92E+02d	1.53E+02d	4.93E-07b	5.92E+05b
dibenzo(a,h)anthracene	53-70-3	2.78E+02a	2.69E+02a	9.16E-08a	6.00E-04a
diuron	330-54-1	2.33E+02a	1.59E+02a	9.20E-05a	4.00E+01a
fluoranthene	206-44-0	2.02E+02a	1.11E+02a	1.23E-03a	2.60E-01a
fluorene	86-73-7	1.66E+02a	1.16E+02a	9.00E-02a	1.90E+00a
indeno(1,2,3-c,d)pyrene	193-39-5	2.76E+02d	1.63E+02d	1.30E-08e	6.20E-02d
naphtalene	91-20-3	1.28E+02a	8.10E+01a	1.04E+01a	3.10E+01a
OCDD	3268-87-9	4.60E+02a	3.22E+02a	1.10E-10a	7.40E-05a
OCDF	39001-02-0	4.44E+02a	2.58E+02a	5.00E-10a	1.16E-06a
oryzalin	19044-88-3	3.46E+02a	1.41E+02a	1.30E-06a	2.40E+00a
oxalate	144-62-7	9.00E+01d	1.98E+02d	3.12E-02d	1.00E+04d
perylene	198-55-0	2.52E+02a	2.77E+02a	1.40E-08a	4.00E-04a
phenanthrene	85-01-8	1.78E+02a	1.01E+02a	1.61E-02a	1.10E+00a
pyrene	129-00-0	2.02E+02a	1.56E+02a	6.12E-04a	1.32E-01a
2,3,7,8-TCDF	51207-31-9	3.06E+02a	2.27E+02a	2.00E-06a	4.19E-04a
total-PAH	-	2.39E+02g	1.96E+02g	2.49E-04g	5.90E-02g
total-PCB	-	3.26E+02i	0.00E+00i	9.00E-04i	2.40E-02i

a = Mackay et al. (1997), b = SRC physprop database (2005), c = PBT profiler (2005), d = Chemfinder (2005), e = Slooff et al. (1989), f = Spectrum laboratories (2005), g = Vermeire (1993; for estimating the ratio between different PAHs), h = Landry et al. (2004), i = Den Hollander and Van de Meent (2004), j = Howard et al. 1991, k = Howard, 1991, l = Karickhoff (1981), m = Bockting et al., 1993.

K_{ow} -	H $Pa.m^3.mol^{-1}$	K_{oc}	kdeg(air) s^{-1}	kdeg(water) s^{-1}	kdeg(soil) s^{-1}
8.32E+03a	1.22E+01a	4.90E+03a	6.93E-05j	6.42E-06j	2.27E-07j
3.47E+04a	3.96E+00a	2.57E+04a	1.94E-04j	1.84E-04j	5.29E-08j
5.62E+02a	2.88E-04a	1.00E+02a	7.41E-05k	1.13E-08a	1.13E-07a
8.13E+05a	5.81E-01a	2.00E+06a	1.11E-04j	1.11E-04j	3.05E-08j
1.10E+06a	4.60E-02a	1.82E+06a	3.02E-04j	3.02E-04j	4.62E-08j
6.31E+05a	3.55E+00a	5.01E+05a	4.26E-05j	2.43E-06j	1.71E-08j
2.51E+07a	2.00E-02a	1.58E+07a	3.51E-06i	1.32E-07i	6.58E-10i
3.16E+06a	7.50E-02a	1.82E+06a	1.90E-04j	1.30E-08j	1.30E-08j
1.00E+06a	1.60E-02	5.50E+05a	5.54E-05j	4.42E-06j	5.75E-09j
4.46E+05a	6.50E-02a	3.16E+05a	7.59E-05j	2.55E-05j	1.32E-08j
2.29E-02b	1.61E-10i	9.39E-03l	3.49E-06c	9.22E-07c	4.72E-07c
5.62E+06a	7.60E-03a	1.66E+06a	1.42E-04j	2.81E-06j	1.38E-08j
6.02E+02a	6.83E-04a	3.98E+02a	1.13E-05a	3.50E-07a	1.13E-07a
1.66E+05a	1.04E+00a	5.50E+04a	3.01E-05j	5.29E-06j	3.23E-08j
1.51E+04a	1.01E+01a	1.41E+04a	8.94E-06j	1.83E-07j	1.83E-07j
3.84E+06f	5.95E-05i	1.57E+06l	9.68E-05j	4.54E-08j	1.21E-08j
2.34E+03a	4.90E+01	9.33E+02m	1.13E-05a	2.54E-06	2.84E-07
1.58E+08a	6.84E-01a	7.94E+07a	3.50E-07a	3.50E-08a	3.44E-09a
1.00E+08a	1.91E-01a	2.51E+07a	3.50E-07a	3.50E-08a	3.50E-09a
5.37E+03a	1.88E-04a	6.02E+02a	1.92E-04f	3.49E-07h	4.01E-07a
1.81E-02d	2.80E-04i	7.42E-03l	5.20E-07	6.42E-06	3.21E-06
1.78E+06a	3.00E-03a	7.30E+05l	1.13E-06a	1.13E-07a	1.13E-08a
2.88E+04a	3.98E+00a	1.66E+04a	3.03E-05j	2.22E-05j	1.42E-07j
1.51E+05a	1.10E+00a	6.61E+04a	1.63E-04j	1.63E-04j	1.27E-08j
1.26E+06a	1.46E+00a	3.16E+07a	2.73E-06j	1.62E-08j	1.62E-08j
1.14E+06g	6.77E-03	1.07E+05g	3.21E-05	1.10E-08	1.10E-08
3.98E+06i	1.22E+01i	1.63E+06l	3.50E-08i	3.50E-09i	3.50E-10i

Appendix A2: Chemical specific input data for SimpleBox.

Profile #	Compound	c_0		d_p	k-factor	c_0		d_p	k-factor
		Fits with a fixed d_p (theoretical model)				Fits without a fixed d_p (regression model)			
1	Citrate	1.41E+01	10^{-6} M	38.1	5.52E+01	2.51E+02	10^{-6} M	5.0	2.85E+00
2	Oxalate	9.29E+00	10^{-6} M	6.7	4.44E+01	2.94E+00	10^{-6} M	14.3	6.11E+01
3	Citrate	1.55E+01	10^{-6} M	38.1	1.41E+01	8.72E+01	10^{-6} M	4.4	1.52E+00
4	Oxalate	7.48E+00	10^{-6} M	6.7	6.04E+00	2.35E+00	10^{-6} M	83.3	1.93E+00
5	Oxalate								
6	Phenanthrene	2.10E+15	10^{-6} g.l^{-1}	1.6	4.54E+15	1.05E+02	10^{-6} g.l^{-1}	41.7	3.12E+00
7	Anthracene	1.42E+06	10^{-6} g.l^{-1}	3.0	3.38E+06	7.06E+00	10^{-6} g.l^{-1}	29.4	5.19E+00
8	Fluoranthene	3.30E+08	10^{-6} g.l^{-1}	3.2	1.12E+07	3.37E+02	10^{-6} g.l^{-1}	24.4	4.00E+00
9	Pyrene	5.70E+05	10^{-6} g.l^{-1}	5.1	1.25E+04	2.04E+02	10^{-6} g.l^{-1}	25.6	3.88E+00
10	Benzo(a)anthracene	9.54E+07	10^{-6} g.l^{-1}	3.3	6.54E+06	1.64E+02	10^{-6} g.l^{-1}	21.7	4.98E+00
11	Chrysene	7.05E+05	10^{-6} g.l^{-1}	5.0	2.06E+04	1.64E+02	10^{-6} g.l^{-1}	28.6	4.20E+00
12	Benzo(k)fluoranthene	5.24E+03	10^{-6} g.l^{-1}	7.7	2.34E+02	5.89E+01	10^{-6} g.l^{-1}	23.8	4.31E+00
13	Benzo(a)pyrene	7.35E+08	10^{-6} g.l^{-1}	2.6	6.57E+08	2.48E+01	10^{-6} g.l^{-1}	25.6	5.08E+00
14	Perylene	2.69E+04	10^{-6} g.l^{-1}	5.4	2.35E+04	5.57E+00	10^{-6} g.l^{-1}	58.8	3.97E+00
15	Indeno(1.2.3-d.c)pyrene	3.02E+05	10^{-6} g.l^{-1}	5.2	7.37E+03	1.69E+02	10^{-6} g.l^{-1}	23.3	3.90E+00
16	Dibenzo(a.h)anthracene	2.33E+05	10^{-6} g.l^{-1}	4.9	3.47E+04	3.48E+01	10^{-6} g.l^{-1}	32.3	4.18E+00
17	Benzo(g.h.i)perylene	4.48E+05	10^{-6} g.l^{-1}	5.0	1.76E+04	1.21E+02	10^{-6} g.l^{-1}	27.8	4.62E+00
18	Naphtalene								
19	Acenaphtene								
20	Fluorene								
21	Phenanthrene	9.93E+15	10^{-6} g.kg^{-1}	1.5	1.43E+15	3.63E+01	10^{-6} g.kg^{-1}	66.7	2.96E+00
22	Anthracene	6.31E+07	10^{-6} g.kg^{-1}	2.5	8.25E+08	1.63E+00	10^{-6} g.kg^{-1}	2.9	6.96E+00
23	Fluoranthene	8.46E+07	10^{-6} g.kg^{-1}	3.1	1.32E+07	1.54E+01	10^{-6} g.kg^{-1}	50.0	5.48E+00
24	Pyrene	1.80E+05	10^{-6} g.kg^{-1}	5.1	2.75E+04	7.23E+00	10^{-6} g.kg^{-1}	250.0	9.63E+00
25	Benzo(a)anthracene	2.21E+05	10^{-6} g.kg^{-1}	3.2	1.64E+05	1.37E+01	10^{-6} g.kg^{-1}	16.1	3.86E+00
26	Chrysene	1.38E+05	10^{-6} g.kg^{-1}	4.9	2.41E+04	8.23E+00	10^{-6} g.kg^{-1}	62.5	1.44E+01
27	Benzo(b)fluoranthene	1.01E+05	10^{-6} g.kg^{-1}	4.3	4.35E+04	1.81E+01	10^{-6} g.kg^{-1}	21.7	8.58E+00
28	Benzo(k)fluoranthene	8.03E+02	10^{-6} g.kg^{-1}	7.6	1.48E+03	2.94E+00	10^{-6} g.kg^{-1}	38.5	1.90E+01
29	Benzo(a)pyrene	1.22E+09	10^{-6} g.kg^{-1}	2.6	4.13E+09	1.66E+01	10^{-6} g.kg^{-1}	27.0	4.38E+00

Profile #	Compound	c_0		d_p	k-factor	c_0		d_p	k-factor
30	Dibenzo(a.h)anthracene	6.48E+04	10^{-6} g.kg^{-1}	4.8	5.88E+05	2.02E+00	10^{-6} g.kg^{-1}	47.6	2.28E+01
31	Benzo(g.h.i)perylene	1.55E+03	10^{-6} g.kg^{-1}	5.0	6.97E+02	1.38E+01	10^{-6} g.kg^{-1}	18.2	3.92E+00
32	Indeno(1.2.3-d.c)pyrene	3.47E+04	10^{-6} g.kg^{-1}	5.2	2.38E+05	2.40E+00	10^{-6} g.kg^{-1}	83.3	1.43E+01
33	Total-PAH	1.77E+03	ng.g^{-1}	5.6	1.77E+00	1.39E+03	ng.g^{-1}	6.3	1.62E+00
34	Total-PCB	2.24E+03	ng.g^{-1}	35.5	2.65E+00	4.13E+03	ng.g^{-1}	9.5	1.71E+00
35	Total-PAH	1.72E+04	ng.g^{-1}	5.6	2.61E+00	9.91E+03	ng.g^{-1}	9.1	1.88E+00
36	Total-PCB	1.79E+03	ng.g^{-1}	35.5	5.98E+00	5.80E+03	ng.g^{-1}	5.6	2.33E+00
37	Total-PAH	2.29E+02	ng.g^{-1}	6.0	2.80E+00	3.38E+02	ng.g^{-1}	4.8	2.42E+00
38	Total-PCB	3.19E+03	ng.g^{-1}	38.5	3.41E+00	5.75E+03	ng.g^{-1}	10.5	2.41E+00
39	Total-PAH	8.34E+02	ng.g^{-1}	6.0	7.11E+00	5.75E+02	ng.g^{-1}	0.9	9.22E+00
40	Total-PCB	1.06E+03	ng.g^{-1}	38.8	2.05E+01	4.87E+03	ng.g^{-1}	5.6	5.95E+00
41	Diuron	1.49E+02	% of dose	2.8	2.59E+01	1.84E+01	% of dose	8.3	2.28E+00
42	Diuron	8.47E+01	% of dose	3.4	1.00E+01	1.99E+01	% of dose	8.3	2.23E+00
43	Oryzalin	1.17E+03	% of dose	1.2	2.49E+03	7.69E+00	% of dose	1.4	1.30E+00
44	Diuron	1.68E+02	% of dose	2.7	2.48E+01	2.12E+01	% of dose	7.7	2.17E+00
45	Oryzalin	6.36E+02	% of dose	1.1	1.48E+02	2.20E+01	% of dose	0.9	1.82E+00
46	Diuron	3.86E+02	% of dose	2.4	3.68E+02	8.86E+00	% of dose	37.0	5.36E+00
47	Oryzalin	1.21E+03	% of dose	1.1	7.83E+02	1.77E+01	% of dose	1.3	3.88E+00
48	Total-PAH	1.39E+01	mg.kg^{-1}	6.4	1.14E+02	9.54E+01	mg.kg^{-1}	1.6	1.97E+01
49	Total-PAH	1.96E+01	mg.kg^{-1}	6.4	3.99E+01	4.20E+01	mg.kg^{-1}	3.5	4.56E+01
50	Total-PAH	1.26E+01	mg.kg^{-1}	6.3	3.11E+01	5.88E+01	mg.kg^{-1}	2.3	7.87E+00
51	Atrazine	5.23E+00	ppm	4.2	1.14E+02	1.99E-01	ppm	12.3	9.83E+00
52	Atrazine	1.81E+01	ppm	4.2	1.23E+03	9.42E-02	ppm	22.7	2.03E+00
53	Atrazine	1.11E+00	ppm	4.2	1.22E+03	1.75E-01	ppm	4.3	3.12E+00
54	Atrazine	2.10E-01	ppm	4.2	5.43E+01	2.78E-02	ppm	5.6	6.94E+01
55	Atrazine	8.85E-01	ppm	4.2	9.12E+01	2.83E-02	ppm	26.7	1.65E+00
56	Atrazine	6.54E+00	ppm	4.2	2.03E+03	2.30E-02	ppm	34.5	1.35E+00
57	Atrazine	2.97E+00	ppm	4.2	1.43E+03	2.97E+00	ppm	1.0	2.04E+00
58	Atrazine	4.13E+00	ppm	4.2	3.87E+03	9.00E-03	ppm	83.3	1.58E+00
59	Atrazine	7.42E+00	ppm	4.2	4.22E+02	1.68E-01	ppm	5.9	3.70E+00
60	Atrazine	1.30E+00	ppm	4.2	4.54E+03	4.20E-03	ppm	2.3	1.60E+00

Profile #	Compound	c_0		d_p	k-factor	c_0		d_p	k-factor
61	OCDD	3.66E+04	$ng.kg^{-1}$	1.0	7.75E+04	6.50E+01	$ng.kg^{-1}$	16.2	1.75E+00
62	OCDF	7.79E+03	$ng.kg^{-1}$	1.0	1.18E+04	4.07E+01	$ng.kg^{-1}$	4.5	3.14E+00
63	2.3.7.8-TCDF	3.83E-02	$ng.kg^{-1}$	4.6	5.61E+05	1.42E+01	$ng.kg^{-1}$	0.9	1.93E+04
64	OCDD	5.33E+04	$ng.kg^{-1}$	1.0	1.67E+05	1.03E+02	$ng.kg^{-1}$	0.9	1.27E+00
65	OCDF	1.39E+04	$ng.kg^{-1}$	1.0	8.38E+04	3.86E+01	$ng.kg^{-1}$	6.3	1.93E+00
66	2.3.7.8-TCDF	6.07E+00	$ng.kg^{-1}$	4.7	3.03E+00	6.69E+00	$ng.kg^{-1}$	4.4	4.68E+00
67	Phenanthrene	4.52E+06	$ng.g^{-1}$	1.7	6.44E+06	1.47E+01	$ng.g^{-1}$	11.1	2.02E+00
68	Fluoranthene	5.98E+03	$ng.g^{-1}$	3.4	1.22E+03	2.00E+01	$ng.g^{-1}$	14.5	2.52E+00
69	Pyrene	3.63E+02	$ng.g^{-1}$	5.4	4.92E+01	1.76E+01	$ng.g^{-1}$	15.9	3.28E+00
70	Benzo(b)fluoranthene	8.98E+02	$ng.g^{-1}$	4.7	7.74E+01	3.00E+01	$ng.g^{-1}$	13.3	3.45E+00
71	Benzo(k)fluoranthene	3.35E+01	$ng.g^{-1}$	8.3	9.86E+00	6.07E+00	$ng.g^{-1}$	19.2	2.73E+00
72	Benzo(a)pyrene	2.04E+04	$ng.g^{-1}$	2.8	6.80E+03	1.74E+01	$ng.g^{-1}$	13.0	3.35E+00
73	Benzo(e)pyrene	5.63E+04	$ng.g^{-1}$	2.6	2.49E+04	1.64E+01	$ng.g^{-1}$	15.8	2.38E+00
74	Benzo(g.h.i)perylene	3.78E+02	$ng.g^{-1}$	5.3	4.51E+01	1.89E+01	$ng.g^{-1}$	14.7	2.66E+00
75	Indeno(1.2.3-d.c)pyrene	2.98E+02	$ng.g^{-1}$	5.5	4.28E+01	1.54E+01	$ng.g^{-1}$	16.0	2.47E+00
76	Phenanthrene	4.08E+06	$ng.g^{-1}$	1.7	1.00E+07	9.35E+00	$ng.g^{-1}$	12.6	2.73E+00
77	Fluoranthene	2.03E+03	$ng.g^{-1}$	3.4	1.91E+02	3.36E+01	$ng.g^{-1}$	3.2	2.77E+00
78	Pyrene	1.95E+02	$ng.g^{-1}$	5.4	1.54E+01	2.46E+01	$ng.g^{-1}$	3.3	2.60E+00
79	Benzo(b)fluoranthene	8.49E+02	$ng.g^{-1}$	4.7	4.70E+01	3.04E+01	$ng.g^{-1}$	11.2	2.39E+00
80	Benzo(k)fluoranthene	4.70E+01	$ng.g^{-1}$	8.3	2.20E+01	4.42E+00	$ng.g^{-1}$	2.6	1.09E+00
81	Benzo(a)pyrene	4.46E+03	$ng.g^{-1}$	2.8	1.79E+03	1.23E+01	$ng.g^{-1}$	3.5	1.87E+00
82	Benzo(e)pyrene	1.03E+04	$ng.g^{-1}$	2.6	2.81E+03	1.99E+01	$ng.g^{-1}$	3.4	2.23E+00
83	Benzo(g.h.i)perylene	1.91E+02	$ng.g^{-1}$	5.3	1.73E+01	2.13E+01	$ng.g^{-1}$	3.4	2.22E+00
84	Indeno(1.2.3-d.c)pyrene	1.50E+02	$ng.g^{-1}$	5.5	1.60E+01	1.76E+01	$ng.g^{-1}$	3.4	2.04E+00

Appendix A3: Calculated d_p, c_0 and uncertainty factors between the measured and the predicted soil concentration profiles. Values are given for the fits with a fixed d_p (theoretical model), and for the fits without a fixed d_p (regression model).

Profile # 1
Country Sweden
Location Nyanget
Compound Citrate
Reference Hees et al., 2005

Depth	Measured C	Theoretical mode	Unit
2,5	116,0	13,7	microM
7,5	76,0	13,4	
15	19,0	13,0	
22,5	1,5	12,7	
27,5	1,5	12,4	

Profile # 2
Country Sweden
Location Nyanget
Compound Oxalate
Reference Hees et al., 2005

Depth	Measured C	Calculated C	Unit
2,5	5,8	6,4	microM
7,5	6,1	3,1	
15	0,0	1,0	
22,5	0,9	0,3	
27,5	1,6	0,2	

Profile # 3
Country Sweden
Location Heden
Compound Citrate
Reference Hees et al., 2005

Depth	Concentration	Calculated C	Unit
1,25	66,00	15,00	microM
3,75	30,00	14,05	
7,5	21,00	12,73	
12,5	4,70	11,16	
17,5	1,50	9,79	

Profile # 4
Country Sweden
Location Heden
Compound Oxalate
Reference Hees et al., 2005

Depth	Concentration	Calculated C	Unit
1,25	2,3	6,2	microM
3,75	1,6	4,3	
7,5	3,3	2,5	
12,5	2,2	1,2	
17,5	1,6	0,6	

Profile # 5
Country Sweden
Location Hasslov
Compound Oxalate
Reference Hees et al., 2005

Depth	Concentration	Calculated C	Unit
1	1,7		microM
3	1,7		
6,5	2,1		
11,5	2,0		
16,5	1,9		

negative soil penetration depth

Profile # 6
Country Germany
Location Hessisches Ried
Compound Phenanthrene
Reference Gocht et al., 2001

Depth	Concentration	Calculated C	Unit
6	164	4,83E+13	10^{-6}g.dm^{-3}
16	118	8,96E+10	
25	38	3,12E+08	
35	30	5,79E+05	
46	34	5,73E+02	
56	8	1,06E+00	
65	24	3,70E-03	
75	22	6,87E-06	
85	16	1,28E-08	
97,5	15	4,91E-12	

Profile # 7
Country Germany
Location Hessisches Ried
Compound Anthracene
Reference Gocht et al., 2001

Depth	Concentration	Calculated C	Unit
6	12	1,93E+05	10^{-6}g.dm^{-3}
16	9	6,87E+03	
25	1	3,42E+02	
35	1	1,22E+01	
46	1	3,12E-01	
56		1,11E-02	
65	1	5,54E-04	
75	1	1,98E-05	

Profile # 8
Country Germany
Location Hessisches Ried
Compound Fluoranthene
Reference Gocht et al., 2001

Depth	Concentration	Calculated C	Unit
6	616,0	4,8E+07	10^{-6}g.dm^{-3}
16	388,0	2,1E+06	
25	61,0	1,3E+05	
35	38,0	5,6E+03	
46	42,0	1,8E+02	
56	12,0	7,9E+00	
65	20,0	4,7E-01	
75	21,0	2,1E-02	
85	13,0	9,1E-04	
97,5	11,0	1,8E-05	

Profile # 9
Country Germany
Location Hessisches Ried
Compound Pyrene
Reference Gocht et al., 2001

Depth	Concentration	Calculated C	Unit
6	375,0	1,8E+05	10^{-6}g.dm^{-3}
16	227,0	2,5E+04	
25	37,0	4,2E+03	
35	24,0	6,0E+02	
46	31,0	6,9E+01	
56	8,0	9,7E+00	
65	15,0	1,7E+00	
75	15,0	2,3E-01	
85	9,0	3,3E-02	
97,5	7,0	2,8E-03	

Profile #	10		
Country	Germany		
Location	Hessisches Ried		
Compound	Benzo(a)anthracene		
Reference	Gocht et al., 2001		
Depth	Concentration	Calculated C	Unit
6	310	1,51E+07	10^{-6}g.dm^{-3}
16	166	6,94E+05	
25	32	4,35E+04	
35	13	2,01E+03	
46	24	6,80E+01	
56	3	3,14E+00	
65	7	1,97E-01	
75	6	9,06E-03	
85	5	4,18E-04	
97,5	4	8,93E-06	

Profile #	11		
Country	Germany		
Location	Hessisches Ried		
Compound	Chrysene		
Reference	Gocht et al., 2001		
Depth	Concentration	Calculated C	Unit
6	278	2,12E+05	10^{-6}g.dm^{-3}
16	239	2,87E+04	
25	37	4,75E+03	
35	26	6,42E+02	
46	25	7,12E+01	
56	7	9,63E+00	
65	15	1,59E+00	
75	14	2,16E-01	
85	13	2,92E-02	
97,5	10	2,39E-03	

Profile #	12		
Country	Germany		
Location	Hessisches Ried		
Compound	Benzo(k)fluoranthene		
Reference	Gocht et al., 2001		
Depth	Concentration	Calculated C	Unit
6	89,0	2,4E+03	10^{-6}g.dm^{-3}
16	86,0	6,5E+02	
25	11,0	2,0E+02	
35	7,0	5,4E+01	
46	7,0	1,3E+01	
56	2,0	3,5E+00	
65	3,0	1,1E+00	
75	2,0	2,9E-01	
85	3,0	7,9E-02	
97,5	2,0	1,6E-02	

Profile #	13		
Country	Germany		
Location	Hessisches Ried		
Compound	Benzo(a)pyrene		
Reference	Gocht et al., 2001		
Depth	Concentration	Calculated C	Unit
6	63,0	7,6E+07	10^{-6}g.dm^{-3}
16	27,0	1,7E+06	
25	4,0	5,7E+04	
35	2,0	1,3E+03	
46	4,0	2,0E+01	
56	1,0	4,5E-01	
65	2,0	1,5E-02	
75	2,0	3,4E-04	
85	1,0	7,6E-06	
97,5	1,0	6,7E-08	

Profile #	14		
Country	Germany		
Location	Hessisches Ried		
Compound	Perylene		
Reference	Gocht et al., 2001		
Depth	Concentration	Calculated C	Unit
6	7	8,88E+03	10^{-6}g.dm^{-3}
16	13	1,40E+03	
25	2	2,65E+02	
35	3	4,17E+01	
46	1	5,46E+00	
56	1	8,60E-01	
65	2	1,63E-01	
75	1	2,57E-02	
85	2	4,04E-03	
97,5	2	4,01E-04	

Profile #	15		
Country	Germany		
Location	Hessisches Ried		
Compound	Indenol(1,2,3-d,c)pyrene		
Reference	Gocht et al., 2001		
Depth	Concentration	Calculated C	Unit
6	270	9,59E+04	10^{-6}g.dm^{-3}
16	180	1,42E+04	
25	37	2,54E+03	
35	17	3,75E+02	
46	23	4,58E+01	
56	5	6,76E+00	
65	7	1,21E+00	
75	9	1,79E-01	
85	5	2,64E-02	
97,5	5	2,42E-03	

Profile #	16		
Country	Germany		
Location	Hessisches Ried		
Compound	dibenzo(a,h)anthracene		
Reference	Gocht et al., 2001		
Depth	Concentration	Calculated C	Unit
6	64,0	6,8E+04	10^{-6}g.dm^{-3}
16	47,0	8,8E+03	
25	7,0	1,4E+03	
35	8,0	1,8E+02	
46	4,0	1,9E+01	
56	5,0	2,4E+00	
65	6,0	3,8E-01	
75	2,0	4,9E-02	
85	2,0	6,4E-03	
97,5	5,0	4,9E-04	

Profile #	17		
Country	Germany		
Location	Hessisches Ried		
Compound	Benzo(g,h,i)perylene		
Reference	Gocht et al., 2001		
Depth	Concentration	Calculated C	Unit
6	247,0	1,4E+05	10^{-6}g.dm^{-3}
16	148,0	1,9E+04	
25	26,0	3,1E+03	
35	17,0	4,3E+02	
46	20,0	4,9E+01	
56	6,0	6,7E+00	
65	5,0	1,1E+00	
75	12,0	1,5E-01	
85	9,0	2,1E-02	
97,5	7,0	1,8E-03	

Profile #	18		
Country	Germany		
Location	Bonn		
Compound	Naphtalene		
Reference	Atanassova & Brummer		
Depth	Concentration	Calculated C	Unit
2,5	0,9		10^{-6}g.kg^{-1}
27,5	0,3		
47,5	0,2		
52	0,4		
65,5	0,4		
78,5	1,3		
91	1,4		

negative soil penetration depth

Profile #	19		
Country	Germany		
Location	Bonn		
Compound	Acenaphtene		
Reference	Atanassova & Brummer		
Depth	Concentration	Calculated C	Unit
2,5	1,3		10^{-6}g.kg^{-1}
27,5	0,6		
47,5	0,3		
52	2		
65,5	0,7		
78,5	1,7		
91	4,9		
negative soil penetration depth			

Profile #	20		
Country	Germany		
Location	Bonn		
Compound	Fluorene		
Reference	Atanassova & Brummer		
Depth	Concentration	Calculated C	Unit
2,5	4,4		10^{-6}g.kg^{-1}
27,5	1,1		
47,5	0,4		
52	6,3		
65,5	1,3		
78,5	3,2		
91	11,0		
negative soil penetration depth			

Profile #	21		
Country	Germany		
Location	Bonn		
Compound	Phenanthrene		
Reference	Atanassova & Brummer		
Depth	Concentration	Calculated C	Unit
2,5	58,0	1,9E+15	10^{-6}g.kg^{-1}
27,5	20,0	1,6E+08	
47,5	7,0	3,3E+02	
52	26,0	1,7E+01	
65,5	9,1	2,5E-03	
78,5	10,0	5,2E-07	

Profile #	22		
Country	Germany		
Location	Bonn		
Compound	Anthracene		
Reference	Atanassova & Brummer		
Depth	Concentration	Calculated C	Unit
2,5	1,6	2,31E+07	10^{-6}g.kg^{-1}
27,5	0,9	1,01E+03	
47,5	0,2	3,28E-01	
52	2,9	5,38E-02	
65,5	0,5	2,38E-04	
78,5	0,3	1,28E-06	

Profile #	23		
Country	Germany		
Location	Bonn		
Compound	Fluoranthene		
Reference	Atanassova & Brummer		
Depth	Concentration	Calculated C	Unit
2,5	21	3,82E+07	10^{-6}g.kg^{-1}
27,5	11	1,33E+04	
47,5	1,2	2,28E+01	
52	8,8	5,44E+00	
65,5	3,8	7,38E-02	
78,5	4,3	1,17E-03	

Profile #	24		
Country	Germany		
Location	Bonn		
Compound	Pyrene		
Reference	Atanassova & Brummer		
Depth	Concentration	Calculated C	Unit
2,5	17,0	1,1E+05	10^{-6}g.kg^{-1}
27,5	10,0	7,8E+02	
47,5	0,7	1,5E+01	
52	8,4	6,1E+00	
65,5	2,2	4,2E-01	
78,5	6,3	3,2E-02	

Profile #	25		
Country	Germany		
Location	Bonn		
Compound	Benzo(a)anthracene		
Reference	Atanassova & Brummer		
Depth	Concentration	Calculated C	Unit
2,5	9,4	1,0E+05	10^{-6}g.kg^{-1}
27,5	5,2	4,3E+01	
47,5	0,3	8,7E-02	
52	0,6	2,1E-02	
65,5	0,3	3,2E-04	

Profile #	26		
Country	Germany		
Location	Bonn		
Compound	Chrysene		
Reference	Atanassova & Brummer		
Depth	Concentration	Calculated C	Unit
2,5	19	8,31E+04	10^{-6}g.kg^{-1}
27,5	8,2	5,27E+02	
47,5	0,3	9,20E+00	
52	5,1	3,70E+00	
65,5	1,9	2,41E-01	
78,5	3,7	1,73E-02	

Profile #	27		
Country	Germany		
Location	Bonn		
Compound	Benzo(b)fluoranthene		
Reference	Atanassova & Brummer		
Depth	Concentration	Calculated C	Unit
2,5	20	5,66E+04	10^{-6}g.kg^{-1}
27,5	9,5	1,76E+02	
47,5	0,4	1,74E+00	
52	1,9	6,14E-01	
65,5		2,72E-02	
78,5	1	1,35E-03	

Profile # 28
Country Germany
Location Bonn
Compound Benzo(k)fluoranthene
Reference Atanassova & Brummer

Depth	Concentration	Calculated C	Unit
2,5	5,1	5,8E+02	10^{-6}g.kg^{-1}
27,5	2,7	2,1E+01	
47,5	0,1	1,5E+00	
52		8,3E-01	
65,5		1,4E-01	
78,5	0,4	2,5E-02	

Profile # 29
Country Germany
Location Bonn
Compound Benzo(a)pyrene
Reference Atanassova & Brummer

Depth	Concentration	Calculated C	Unit
2,5	20,0	4,7E+08	10^{-6}g.kg^{-1}
27,5	6,0	3,2E+04	
47,5	3,9	1,5E+01	
52	1,2	2,7E+00	
65,5		1,5E-02	
78,5	0,4	1,1E-04	
91	1,5	8,8E-07	

Profile # 30
Country Germany
Location Bonn
Compound Dibenzo(a,h)anthracene
Reference Atanassova & Brummer

Depth	Concentration	Calculated C	Unit
2,5	2,3	3,86E+04	10^{-6}g.kg^{-1}
27,5	1,2	2,16E+02	
47,5	0,4	3,40E+00	
52	0,9	1,34E+00	
65,5	0,4	8,13E-02	
78,5	0,6	5,48E-03	
91	29	4,10E-04	

Profile # 31
Country Germany
Location Bonn
Compound Benzo(g,h,i)perylene
Reference Atanassova & Brummer

Depth	Concentration	Calculated C	Unit
2,5	10	9,37E+02	10^{-6}g.kg^{-1}
27,5	5,1	6,25E+00	
47,5	0,5	1,14E-01	
52	1,2	4,61E-02	

Profile # 32
Country Germany
Location Bonn
Compound indenol(1,2,3-c,d)pyrene
Reference Atanassova & Brummer

Depth	Concentration	Calculated C	Unit
2,5	9,8	2,1E+04	10^{-6}g.kg^{-1}
27,5	0,5	1,7E+02	
47,5	0,5	3,5E+00	
52	1,2	1,5E+00	
65,5		1,1E-01	
78,5		8,6E-03	
91	2,1	7,6E-04	

Profile # 33
Country United Kingdom
Location Park Grass
Compound Total-PAH
Reference Cousins et al., 1999

Depth	Concentration	Calculated C	Unit
1	700,0	1,5E+03	ng.g-1
2	1050,0	1,2E+03	
3	1120,0	1,0E+03	
4	800,0	8,6E+02	
5	850,0	7,2E+02	
7	450,0	5,0E+02	
9	400,0	3,5E+02	
11	350,0	2,4E+02	
13	200,0	1,7E+02	
15	120,0	1,2E+02	
17	100,0	8,3E+01	

Profile # 34
Country United Kingdom
Location Park Grass
Compound Total-PCB
Reference Cousins et al., 1999

Depth	Concentration	Calculated C	Unit
1	3100	2,18E+03	ng.g-1
2	3000	2,12E+03	
3	4200	2,06E+03	
4	3300	2,00E+03	
5	2950	1,95E+03	
7	1500	1,84E+03	
9	1200	1,74E+03	
11	1500	1,64E+03	
13	1000	1,55E+03	
15	600	1,47E+03	
17	1000	1,39E+03	

Profile # 35
Country United Kingdom
Location Broadbalk
Compound Total-PAH
Reference Cousins et al., 1999

Depth	Concentration	Calculated C	Unit
1	7300	1,44E+04	ng.g-1
2	7300	1,20E+04	
3	8200	1,00E+04	
4	7600	8,38E+03	
5	6500	7,00E+03	
7	5900	4,88E+03	
9	4000	3,40E+03	
11	2000	2,37E+03	
13	1500	1,66E+03	
15	1500	1,15E+03	
17	2700	8,05E+02	

Profile # 36
Country United Kingdom
Location Broadbalk
Compound Total-PCB
Reference Cousins et al., 1999

Depth	Concentration	Calculated C	Unit
1	6200,0	1,7E+03	pg.g-1
2	5900,0	1,7E+03	
3	5300,0	1,6E+03	
4	2000,0	1,6E+03	
5	1400,0	1,6E+03	
7	1600,0	1,5E+03	
9	900,0	1,4E+03	
11	900,0	1,3E+03	
13	300,0	1,2E+03	
15	500,0	1,2E+03	
17	500,0	1,1E+03	

Profile # 37
Country United Kingdom
Location Glengsaugh
Compound Total-PAH
Reference Cousins et al., 1999

Depth	Concentration	Calculated C	Unit
1	230,0	1,9E+02	ng.g-1
2	240,0	1,6E+02	
3	250,0	1,4E+02	
4	290,0	1,2E+02	
5	155,0	9,9E+01	
7	45,0	7,1E+01	
9	30,0	5,0E+01	
11	20,0	3,6E+01	
13	15,0	2,6E+01	
17	10,0	1,3E+01	
22	5,0	5,7E+00	

Profile # 38
Country United Kingdom
Location Glengsaugh
Compound Total-PCB
Reference Cousins et al., 1999

Depth	Concentration	Calculated C	Unit
1	10000	3,11E+03	pg.g-1
2	8200	3,03E+03	
3	5300	2,96E+03	
4	3200	2,88E+03	
5	2000	2,81E+03	
7	1700	2,66E+03	
9	1750	2,53E+03	
11	1600	2,40E+03	
13	1550	2,28E+03	
17	1500	2,05E+03	
22	1000	1,80E+03	

Profile # 39
Country United Kingdom
Location Hartwood
Compound Total-PAH
Reference Cousins et al., 1999

Depth	Concentration	Calculated C	Unit
1	200	7,05E+02	ng.g-1
2	950	5,97E+02	
3	1050	5,05E+02	
4	1100	4,28E+02	
5	150	3,62E+02	

Profile # 40
Country United Kingdom
Location Hartwood
Compound Total_PCB
Reference Cousins et al., 1999

Depth	Concentration	Calculated C	Unit
1	1600,0	1,0E+03	pg.g-1
2	7300,0	1,0E+03	
3	9000,0	9,8E+02	
4	7300,0	9,5E+02	
5	3200,0	9,3E+02	
7	600,0	8,8E+02	
9	500,0	8,4E+02	
11	500,0	8,0E+02	
13	150,0	7,6E+02	
17	150,0	6,8E+02	
22	100,0	6,0E+02	
28	100,0	5,1E+02	

Profile # 41
Country France
Location Burgundy - rendosol
Compound Diuron
Reference Landry et al., 2005

Depth	Concentration	Calculated C	Unit
1,25	24,0	9,5E+01	% of dose
3,75	10,0	3,8E+01	
7,5	6,0	9,8E+00	
12,5	3,0	1,6E+00	
17,5	3,5	2,6E-01	

Profile # 42
Country France
Location Burgundy - calcosol MS
Compound Diuron
Reference Landry et al., 2005

Depth	Concentration	Calculated C	Unit
1,25	28	5,88E+01	% of dose
3,75	9	2,84E+01	
7,5	6	9,51E+00	
12,5	4	2,21E+00	
17,5	3	5,15E-01	

Profile # 43
Country France
Location Burgundy - calcosol MS
Compound Oryzalin
Reference Landry et al., 2005

Depth	Concentration	Calculated C	Unit
1,25	8,0	4,2E+02	% of dose
3,75	6,0	5,3E+01	
7,5	6,5	2,4E+00	
12,5	6,5	3,8E-02	

Profile # 44
Country France
Location Burgundy - calcosol veg
Compound Diuron
Reference Landry et al., 2005

Depth	Concentration	Calculated C	Unit
1,25	29	1,06E+02	% of dose
3,75	10	4,22E+01	
7,5	6	1,06E+01	
12,5	4	1,67E+00	
17,5	3	2,64E-01	

Profile # 45
Country France
Location Burgundy - calcosol veg
Compound Oryzalin
Reference Landry et al., 2005

Depth	Concentration	Calculated C	Unit
1,25	22	2,00E+02	% of dose
3,75	11	1,97E+01	
7,5	10	6,13E-01	

Profile # 46
Country France
Location Burgundy - calcosol bare
Compound Diuron
Reference Landry et al., 2005

Depth	Concentration	Calculated C	Unit
1,25	26	2,29E+02	% of dose
3,75	4	8,09E+01	
7,5	7	1,70E+01	
12,5	12	2,11E+00	
17,5	20	2,63E-01	

Profile # 47
Country France
Location Burgundy - calcosol bare
Compound Oryzalin
Reference Landry et al., 2005

Depth	Concentration	Calculated C	Unit
1,25	9,0	4,0E+02	% of dose
3,75	7,0	3,8E+01	
7,5	6,0	1,2E+00	
12,5	0,5	1,1E-02	

Profile # 48
Country Slovakia
Location Ziar - 1
Compound Total-PAH
Reference Wilcke et al., 1996

Depth	Concentration	Calculated C	Unit
1	93,8	1,2E+01	mg.kg-1
2	73,0	1,0E+01	
3	2,5	8,7E+00	
11	0,2	2,5E+00	

Profile # 49
Country Slovakia
Location Ziar - 2
Compound Total-PAH
Reference Wilcke et al., 1996

Depth	Concentration	Calculated C	Unit
1	84	2,E+01	mg.kg-1
2	71	1,E+01	
3	2	1,E+01	
17	0	1,E+00	

Profile # 50
Country Slovakia
Location Ziar -3
Compound Total-PAH
Reference Wilcke et al., 1996

Depth	Concentration	Calculated C	Unit
1	57	1,E+01	mg.kg-1
2	35	9,E+00	
6	1	5,E+00	
13	0	2,E+00	

Profile # 51
Country Portugal
Location Sorraia Valley - 1
Compound Atrazine
Reference Azevedo et al., 2000

Depth	Concentration	Calculated C	Unit
5	0,3	1,6E+00	ppm
15	0,0	1,5E-01	
25	0,0	1,3E-02	
38	0,0	6,0E-04	

Profile # 52
Country Portugal
Location Sorraia Valley - 2
Compound Atrazine
Reference Azevedo et al., 2000

Depth	Concentration	Calculated C	Unit
5	0,1	5,5E+00	ppm
15	0,0	5,0E-01	
25	0,0	4,6E-02	
38	0,0	2,1E-03	
52	0,0	7,4E-05	

Profile # 53
Country Portugal
Location Sorraia Valley - 3
Compound Atrazine
Reference Azevedo et al., 2000

Depth	Concentration	Calculated C	Unit
5	0,1		ppm
15	0,03		
25	0,01		

Profile # 54
Country Portugal
Location Sorraia Valley - 4
Compound Atrazine
Reference Azevedo et al., 2000

Depth	Concentration	Calculated C	Unit
5	0,04	6,36E-02	ppm
15	0,001	5,85E-03	
25	0,005	5,38E-04	

Profile # 55
Country Portugal
Location Sorraia Valley -5
Compound Atrazine
Reference Azevedo et al., 2000

Depth	Concentration	Calculated C	Unit
5	0,03	2,7E-01	ppm
15	0,02	2,5E-02	
25	0,03	2,3E-03	

Profile # 56
Country Portugal
Location Sorraia Valley - 6
Compound Atrazine
Reference Azevedo et al., 2000

Depth	Concentration	Calculated C	Unit
5	0,02	2,0E+00	ppm
15	0,01	1,8E-01	
25	0,01	1,7E-02	
38	0,01	7,5E-04	
52	0,01	2,7E-05	

Profile # 57
Country Portugal
Location Sorraia Valley - 7
Compound Atrazine
Reference Azevedo et al., 2000

Depth	Concentration	Calculated C	Unit
5	0,015	8,99E-01	ppm
15	0,011	8,27E-02	
25	0,003	7,60E-03	
38		3,42E-04	
52	0,001	1,21E-05	

Profile # 58
Country Portugal
Location Sorraia Valley - 8
Compound Atrazine
Reference Azevedo et al., 2000

Depth	Concentration	Calculated C	Unit
5	0,009	1,25E+00	ppm
15	0,006	1,15E-01	
25	0,009	1,06E-02	
38	0,005	4,75E-04	
52	0,005	1,68E-05	

Profile # 59
Country Portugal
Location Sorraia Valley - 9
Compound Atrazine
Reference Azevedo et al., 2000

Depth	Concentration	Calculated C	Unit
5	0,2	2,2E+00	ppm
15	0,0	2,1E-01	
25		1,9E-02	
38	0,0	8,5E-04	

Profile # 60
Country Portugal
Location Sorraia Valley - 12
Compound Atrazine
Reference Azevedo et al., 2000

Depth	Concentration	Calculated C	Unit
5	0,004	3,93E-01	ppm
15	0,003	3,61E-02	
25	0,0015	3,32E-03	
38		1,49E-04	
52	0,001	5,28E-06	

Profile # 61
Country Germany
Location Starnberg
Compound OCDD
Reference Rotard et al., 1994

Depth	Concentration	Calculated C	Unit
1	75,0	1,3E+04	ng.kg-1
3,5	50,0	1,1E+03	
7,5	30,0	2,0E+01	
15	30,0	1,1E-02	

Profile # 62
Country Germany
Location Starnberg
Compound OCDF
Reference Rotard et al., 1994

Depth	Concentration	Calculated C	Unit
1	48	2,86E+03	ng.kg-1
3,5	18	2,35E+02	
7,5	4	4,31E+00	
15	2	2,38E-03	

Profile # 63
Country Germany
Location Starnberg
Compound 2,3,7,8-TCDF
Reference Rotard et al., 1994

Depth	Concentration	Calculated C	Unit
1	9	3,08E-02	ng.kg-1
3,5	7	1,80E-02	
7,5	1,00E-05	7,58E-03	
15	1,00E-05	1,50E-03	

Profile # 64
Country Germany
Location Schauinsland
Compound OCDD
Reference Rotard et al., 1994

Depth	Concentration	Calculated C	Unit
1	87,0	2,0E+04	ng.kg-1
5,5	63,0	2,2E+02	
14,5	21,0	2,7E-02	

Profile # 65
Country Germany
Location Schauinsland
Compound OCDF
Reference Rotard et al., 1994

Depth	Concentration	Calculated C	Unit
1	27,5	5,1E+03	ng.kg-1
5,5	21,0	5,7E+01	
14,5	3,5	7,0E-03	

Profile # 66
Country Germany
Location Schauinsland
Compound 2,3,7,8-TCDF
Reference Rotard et al., 1994

Depth	Concentration	Calculated C	Unit
1	3,5	4,90E+00	ng.kg-1
5,5	3,6	1,87E+00	
14,5	0,2	2,74E-01	

Profile # 67
Country Denmark
Location Ejby
Compound Phenanthrene
Reference Vikelsoe et al., 2002

Depth	Concentration	Calculated C	Unit
5	13	2,26E+05	ng.g-1
15	3	5,68E+02	
25	1	1,42E+00	
35	0,5	3,57E-03	
45	0,3	8,96E-06	

Profile # 68
Country Denmark
Location Ejby
Compound Fluoranthene
Reference Vikelsoe et al., 2002

Depth	Concentration	Calculated C	Unit
5	16,5	1,4E+03	ng.g-1
15	8,0	7,0E+01	
25	3,0	3,6E+00	
35	1,0	1,8E-01	
45	1,5	9,5E-03	

Profile # 69
Country Denmark
Location Ejby
Compound Pyrene
Reference Vikelsoe et al., 2002

Depth	Concentration	Calculated C	Unit
5	17,0	1,4E+02	ng.g-1
15	7,5	2,3E+01	
25	2,5	3,6E+00	
35	1,0	5,8E-01	
45	2,0	9,1E-02	

Profile # 70
Country Denmark
Location Ejby
Compound Benzo(b)fluoranthene
Reference Vikelsoe et al., 2002

Depth	Concentration	Calculated C	Unit
5	24,5	3,13E+02	ng.g-1
15	12	3,79E+01	
25	3,5	4,60E+00	
35	1	5,58E-01	
45	2	6,76E-02	

Profile # 71
Country Denmark
Location Ejby
Compound Benzo(k)fluoranthene
Reference Vikelsoe et al., 2002

Depth	Concentration	Calculated C	Unit
5	5,5	1,84E+01	ng.g-1
15	3	5,51E+00	
25	1,5	1,65E+00	
35	0,5	4,96E-01	
45	1	1,49E-01	

Profile # 72
Country Denmark
Location Ejby
Compound Benzo(a)pyrene
Reference Vikelsoe et al., 2002

Depth	Concentration	Calculated C	Unit
5	13,0	3,4E+03	ng.g-1
15	6,5	9,3E+01	
25	2,5	2,5E+00	
35	0,5	7,0E-02	
45	1,0	1,9E-03	

Profile # 73
Country Denmark
Location Ejby
Compound Benzo(e)pyrene
Reference Vikelsoe et al., 2002

Depth	Concentration	Calculated C	Unit
5	13,5	8,0E+03	ng.g-1
15	7,0	1,6E+02	
25	3,0	3,4E+00	
35	1,0	6,9E-02	
45	1,5	1,4E-03	

Profile # 74
Country Denmark
Location Ejby
Compound Benzo(g,h,i)perylene
Reference Vikelsoe et al., 2002

Depth	Concentration	Calculated C	Unit
5	16	1,48E+02	ng.g-1
15	8	2,25E+01	
25	2,5	3,44E+00	
35	1	5,25E-01	
45	1,5	8,01E-02	

Profile # 75
Country Denmark
Location Ejby
Compound Indeno(1,2,3-c,d)pyrene
Reference Vikelsoe et al., 2002

Depth	Concentration	Calculated C	Unit
5	13	1,20E+02	ng.g-1
15	7	1,97E+01	
25	2,5	3,21E+00	
35	1	5,25E-01	
45	1,5	8,57E-02	

Profile # 76
Country Denmark
Location Sundbylille
Compound Phenanthrene
Reference Vikelsoe et al., 2002

Depth	Concentration	Calculated C	Unit
5	4,0	2,0E+05	ng.g-1
15	3,5	5,1E+02	
25	2,5	1,3E+00	
35	0,5	3,2E-03	
45	0,2	8,1E-06	

Profile # 77
Country Denmark
Location Sundbylille
Compound Fluoranthene
Reference Vikelsoe et al., 2002

Depth	Concentration	Calculated C	Unit
5	17,5	4,7E+02	ng.g-1
15	9,0	2,5E+01	
25	6,5	1,3E+00	
35	1,0	6,9E-02	

Profile # 78
Country Denmark
Location Sundbylille
Compound Pyrene
Reference Vikelsoe et al., 2002

Depth	Concentration	Calculated C	Unit
5	13	7,75E+01	ng.g-1
15	8	1,23E+01	
25	5,5	1,95E+00	
35	1	3,09E-01	

Profile # 79
Country Denmark
Location Sundbylille
Compound Benzo(b)fluoranthene
Reference Vikelsoe et al., 2002

Depth	Concentration	Calculated C	Unit
5	18	2,96E+02	ng.g-1
15	11,5	3,58E+01	
25	7,5	4,35E+00	
35	2	5,27E-01	
45	0,5	6,39E-02	

Profile # 80
Country Denmark
Location Sundbylille
Compound Benzo(k)fluoranthene
Reference Vikelsoe et al., 2002

Depth	Concentration	Calculated C	Unit
5	4,0	19,0	ng.g-1
15	3,0	3,1	
25	2,5	0,5	

Profile # 81
Country Denmark
Location Sundbylille
Compound Benzo(a)pyrene
Reference Vikelsoe et al., 2002

Depth	Concentration	Calculated C	Unit
5	8,0	7,4E+02	ng.g-1
15	4,5	2,0E+01	
25	3,5	5,5E-01	
35	1,0	1,5E-02	

Profile #	82		
Country	Denmark		
Location	Sundbylille		
Compound	Benzo(e)pyrene		
Reference	Vikelsoe et al., 2002		
Depth	Concentration	Calculated C	Unit
5	11	1,48E+03	ng.g-1
15	7	3,02E+01	
25	4,5	6,17E-01	
35	1	1,26E-02	

Profile #	83		
Country	Denmark		
Location	Sundbylille		
Compound	Benzo(g,h,i)perylene		
Reference	Vikelsoe et al., 2002		
Depth	Concentration	Calculated C	Unit
5	11,5	7,44E+01	ng.g-1
15	7,5	1,14E+01	
25	4,5	1,73E+00	
35	1	2,65E-01	

Profile #	84		
Country	Denmark		
Location	Sundbylille		
Compound	Indeno(1,2,3-c,d)pyrene		
Reference	Vikelsoe et al., 2002		
Depth	Concentration	Calculated C	Unit
5	10,0	6,1E+01	ng.g-1
15	6,5	9,9E+00	
25	4,0	1,6E+00	
35	1,0	2,7E-01	

Appendix A4 (p. 157-165): Tables of the measured data points and the calculated soil concentration profiles from the theoretical model of Equation 5.

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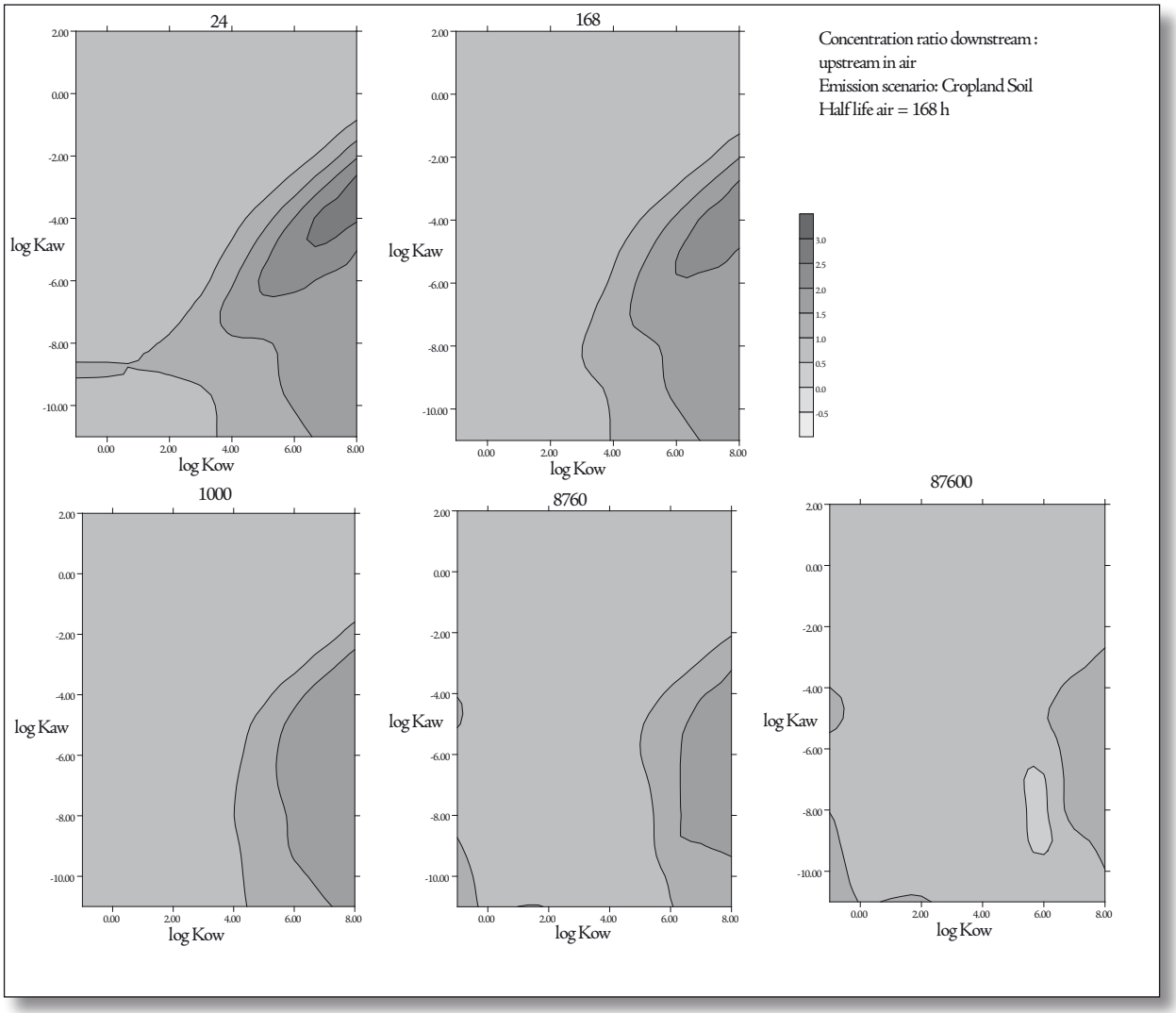
Appendix B: Supporting information 'BasinBox, a generic multimedia fate model for predicting the environmental fate of chemicals in river basins'

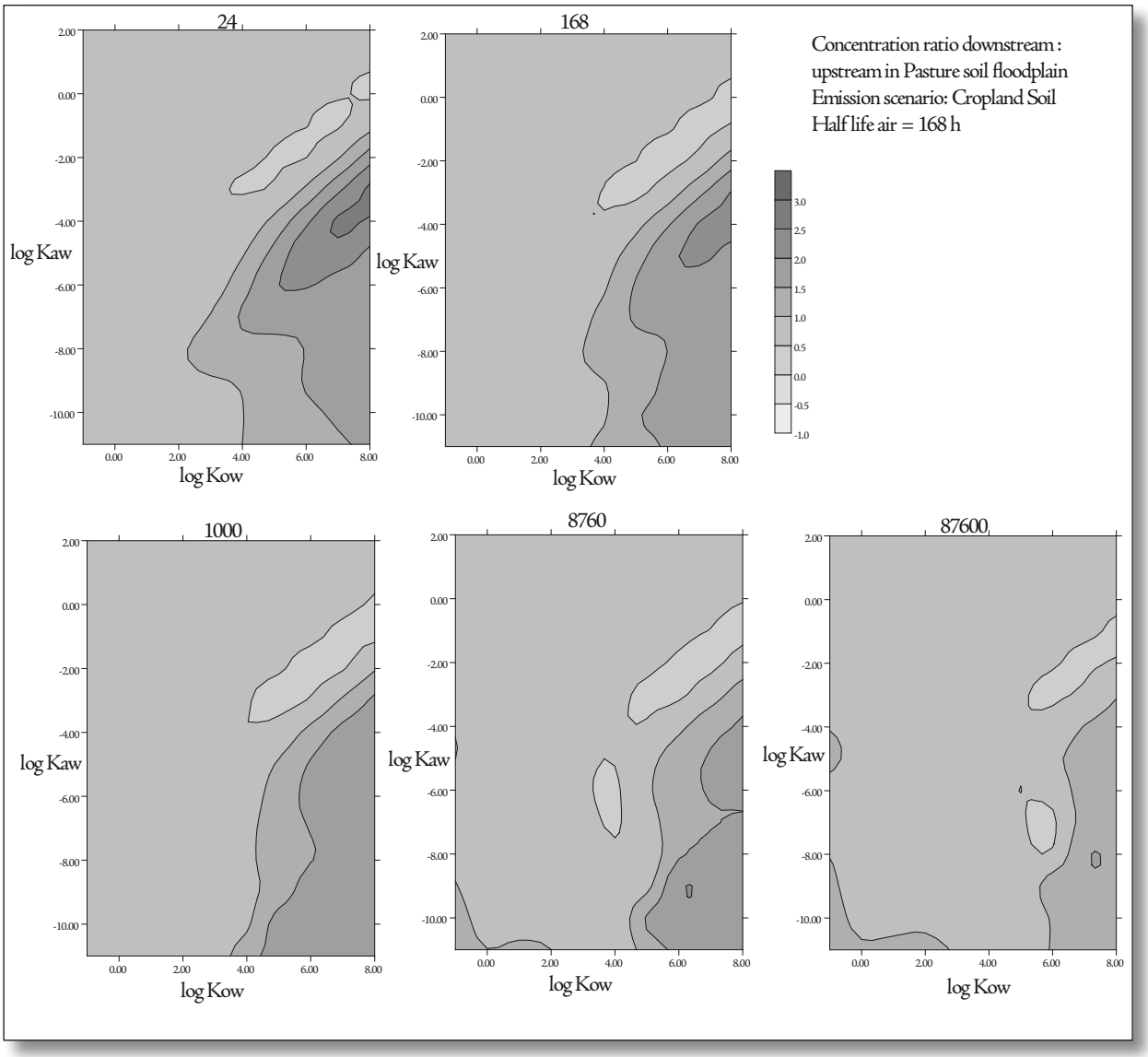
Chemical space plots for the combinations of emission scenario and compartment type for which concentration ratios >100 were predicted between the downstream and upstream area of the river Rhine basin. In the plots, log K_{ow}-values are plotted against log K_{aw}-values.

For each of these scenarios, five separate plots are given for all five modeled values of the degradation half-life in water (4, 24, 168, 1000 and 8760 h). For all plots a degradation half-life in air of 168 h, and unit emissions towards the cropland soil compartment apply.

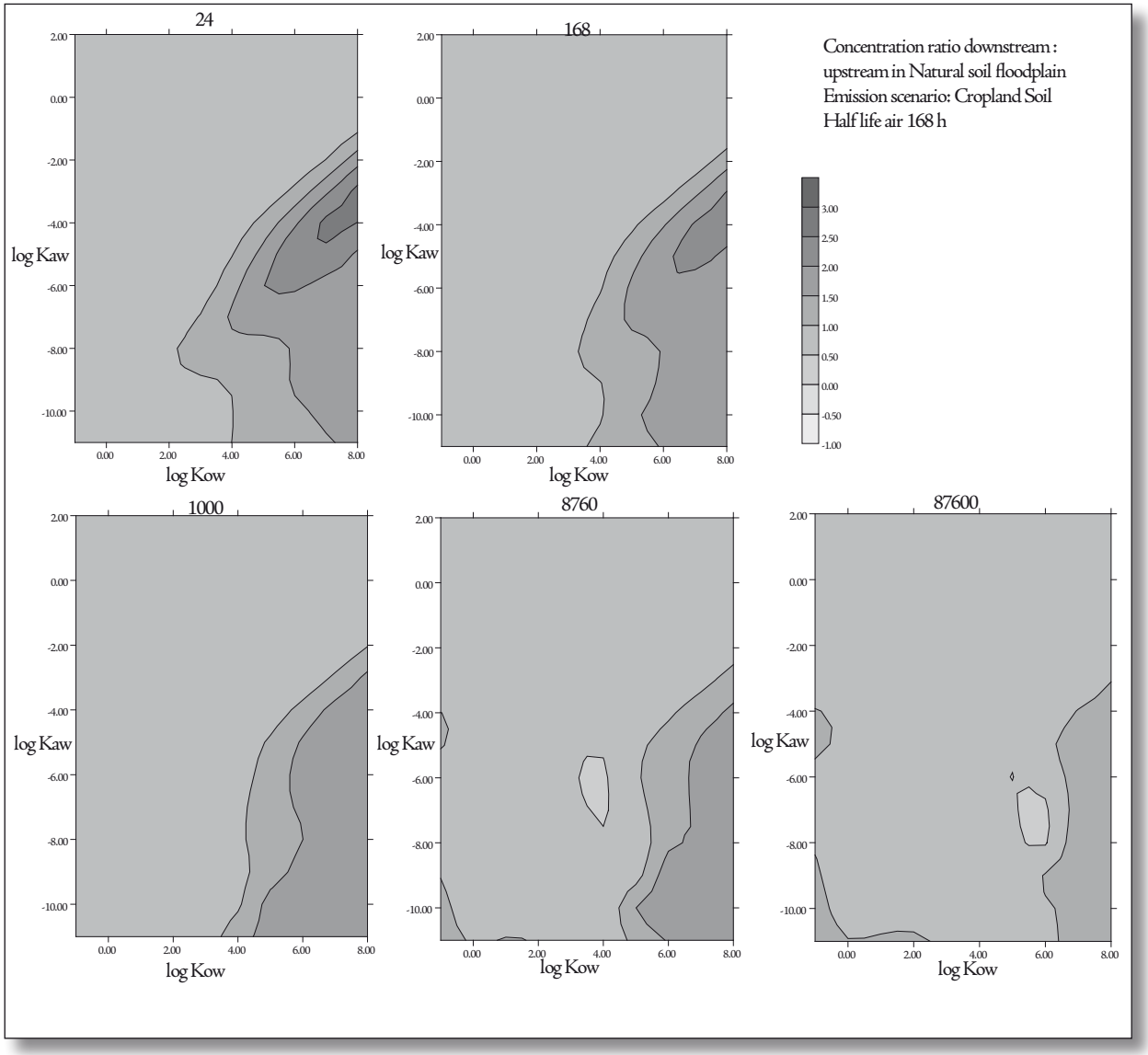
Appendix B1: air compartment,
Appendix B2: pasture soil floodplain,
Appendix B3: natural soil floodplain,
Appendix B4: pasture vegetation floodplain,
Appendix B5: cropland vegetation floodplain,
Appendix B6: natural vegetation floodplain,
Appendix B7: pasture soil catchment,
Appendix B8: natural soil catchment,
Appendix B9: pasture vegetation catchment,
Appendix B10: cropland vegetation catchment,
Appendix B11: natural vegetation catchment.


24
168
1000
8760
87600
log Kaw
log Kow
Concentration ratio downstream : upstream in air
Emission scenario: Cropland Soil
Half life air = 168 h
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

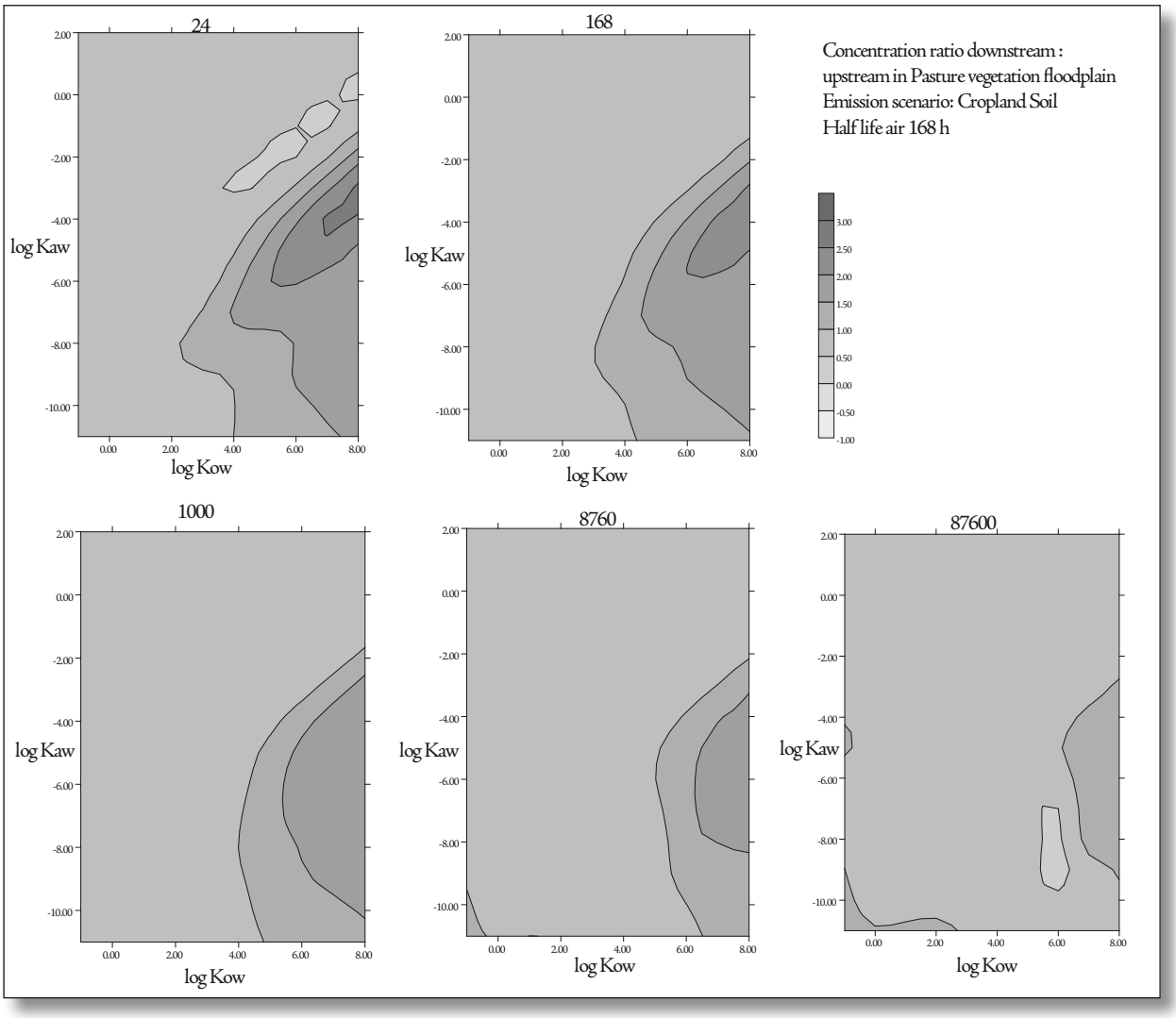
Appendix B1


24
168
1000
8760
87600
log Kaw
log Kow
Concentration ratio downstream : upstream in Pasture soil floodplain
Emission scenario: Cropland Soil
Half life air = 168 h
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

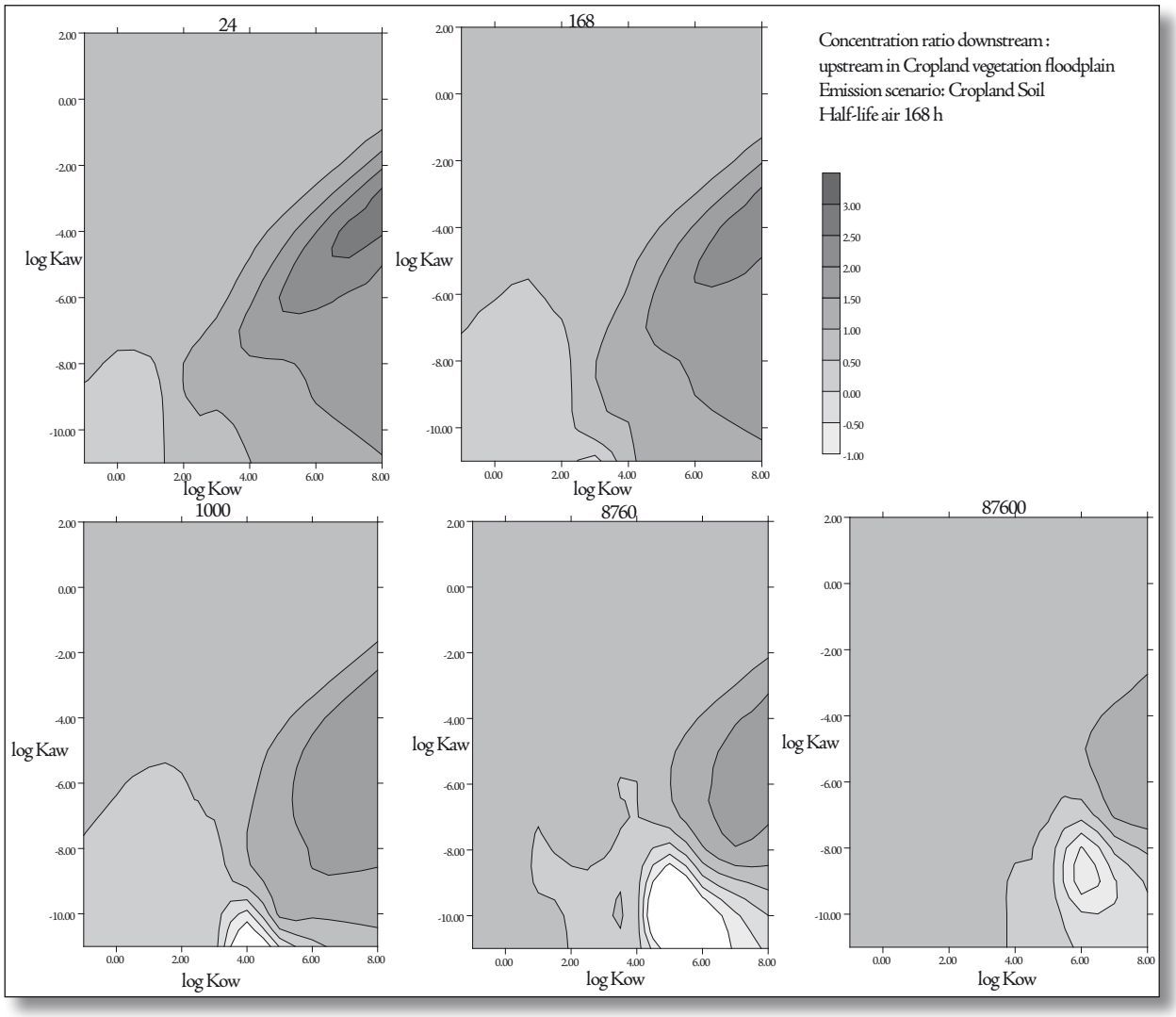
Appendix B2


24
168
1000
8760
87600
log Kaw
log Kow
2.00
0.00
-2.00
-4.00
-6.00
-8.00
-10.00
0.00
2.00
4.00
6.00
8.00
Concentration ratio downstream : upstream in Natural soil floodplain
Emission scenario: Cropland Soil
Half life air 168 h
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00

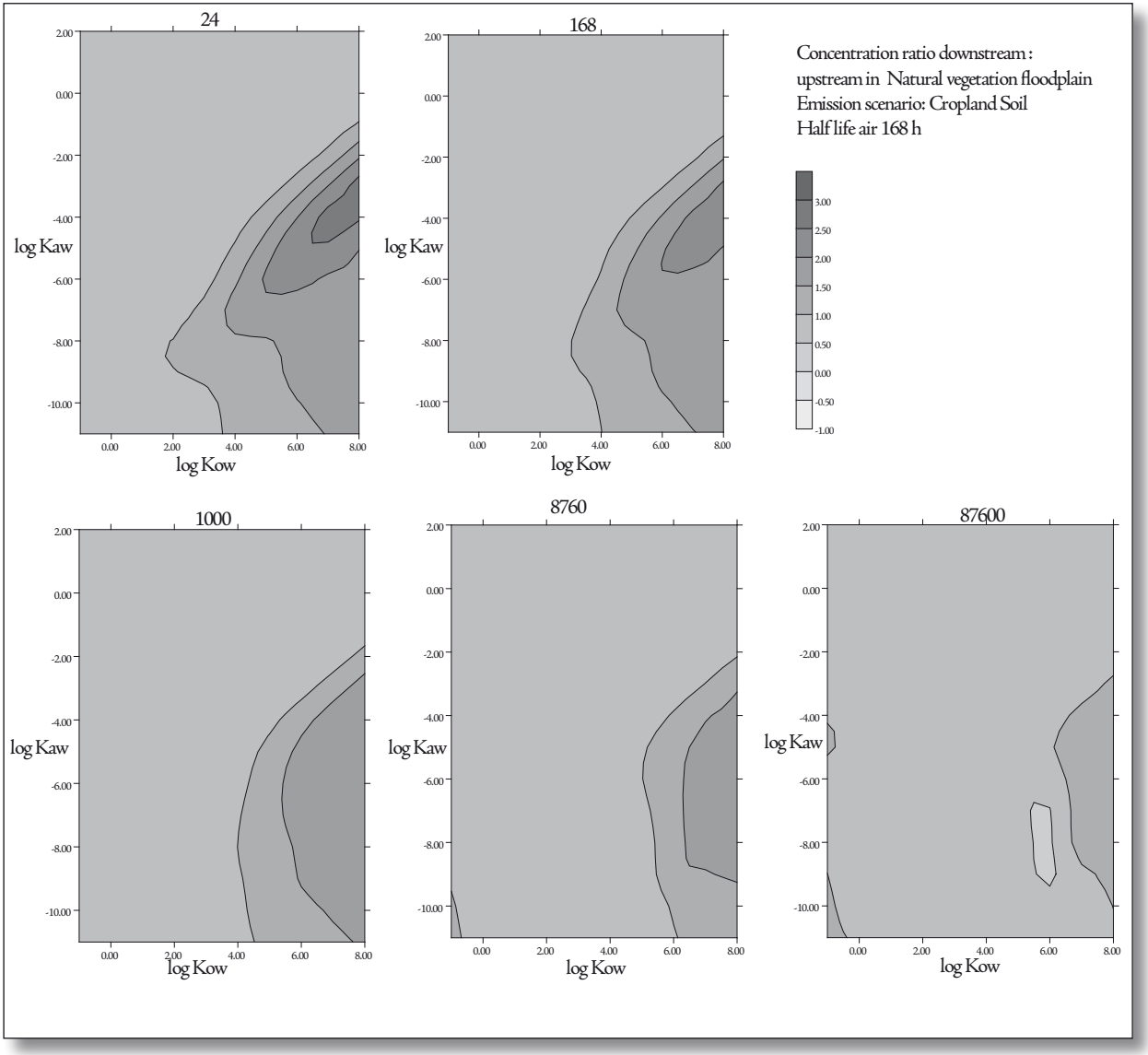
Appendix B3


24
168
1000
8760
87600
log Kaw
log Kow
Concentration ratio downstream : upstream in Pasture vegetation floodplain
Emission scenario: Cropland Soil
Half life air 168 h
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00

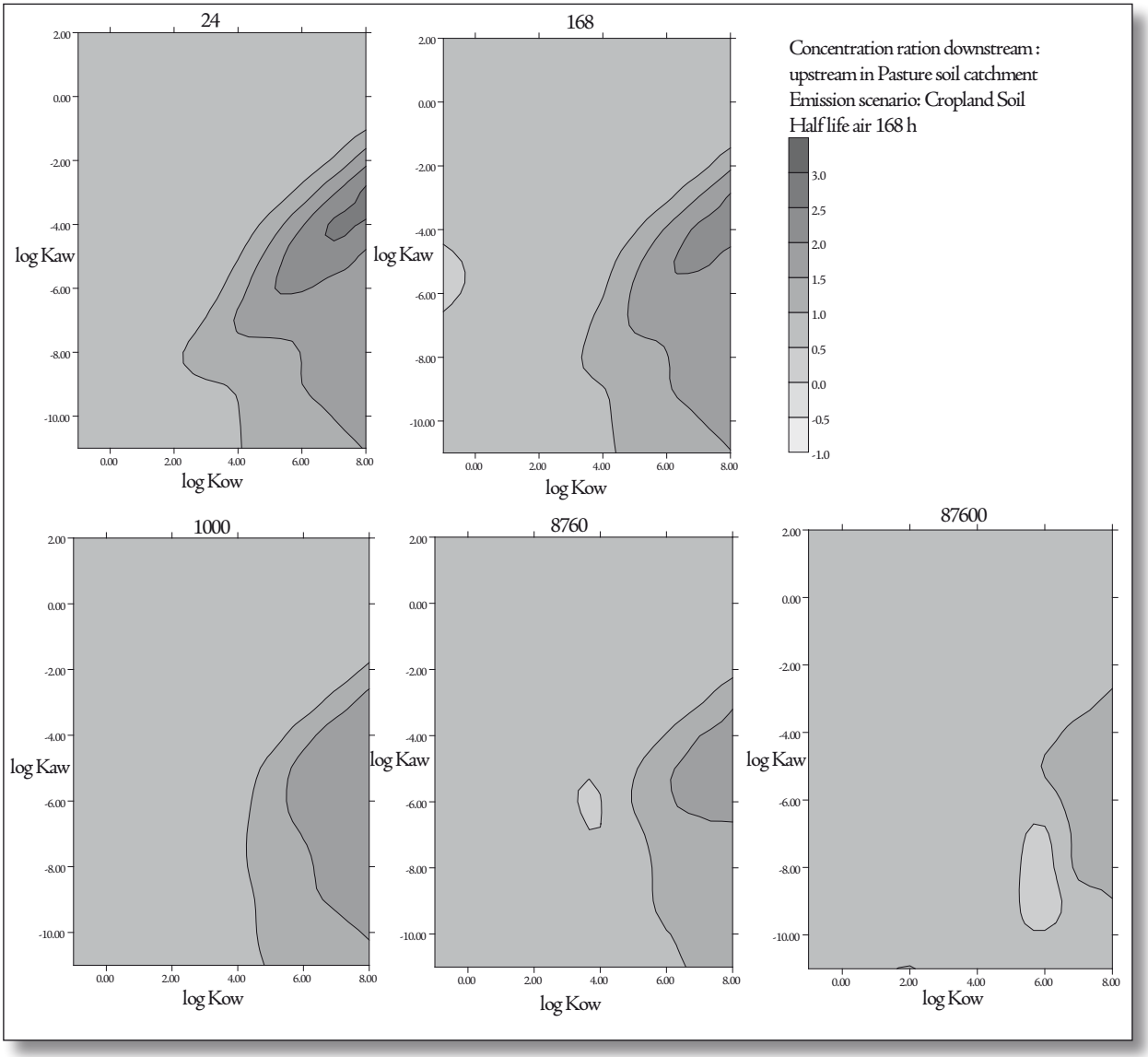
Appendix B4


24
168
1000
8760
87600
Concentration ratio downstream :
upstream in Cropland vegetation floodplain
Emission scenario: Cropland Soil
Half-life air 168 h
log Kaw
log Kow
2.00
0.00
-2.00
-4.00
-6.00
-8.00
-10.00
0.00
2.00
4.00
6.00
8.00
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00

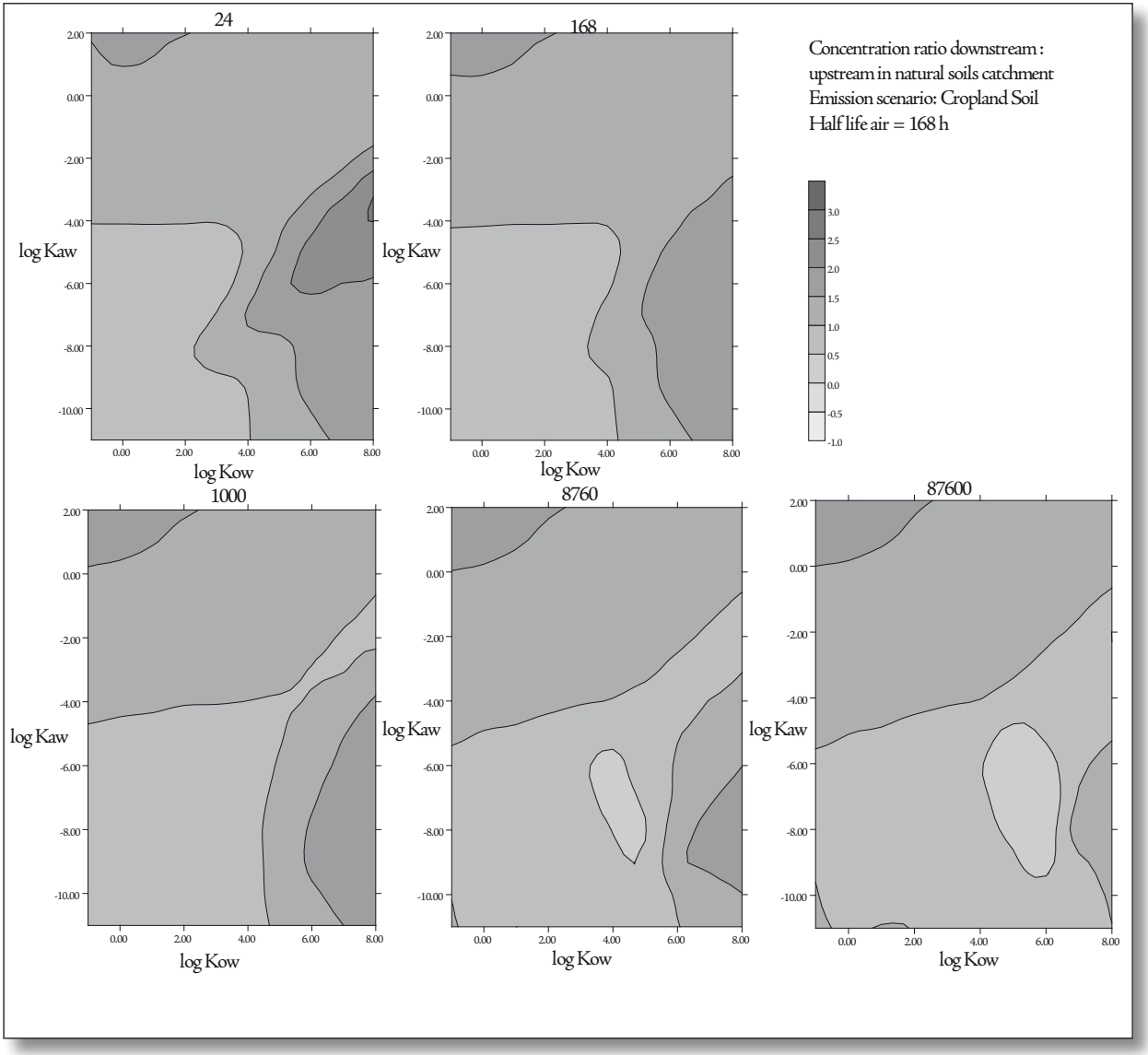
Appendix B5


24
168
1000
8760
87600
log Kaw
log Kow
Concentration ratio downstream : upstream in Natural vegetation floodplain
Emission scenario: Cropland Soil
Half life air 168 h
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00

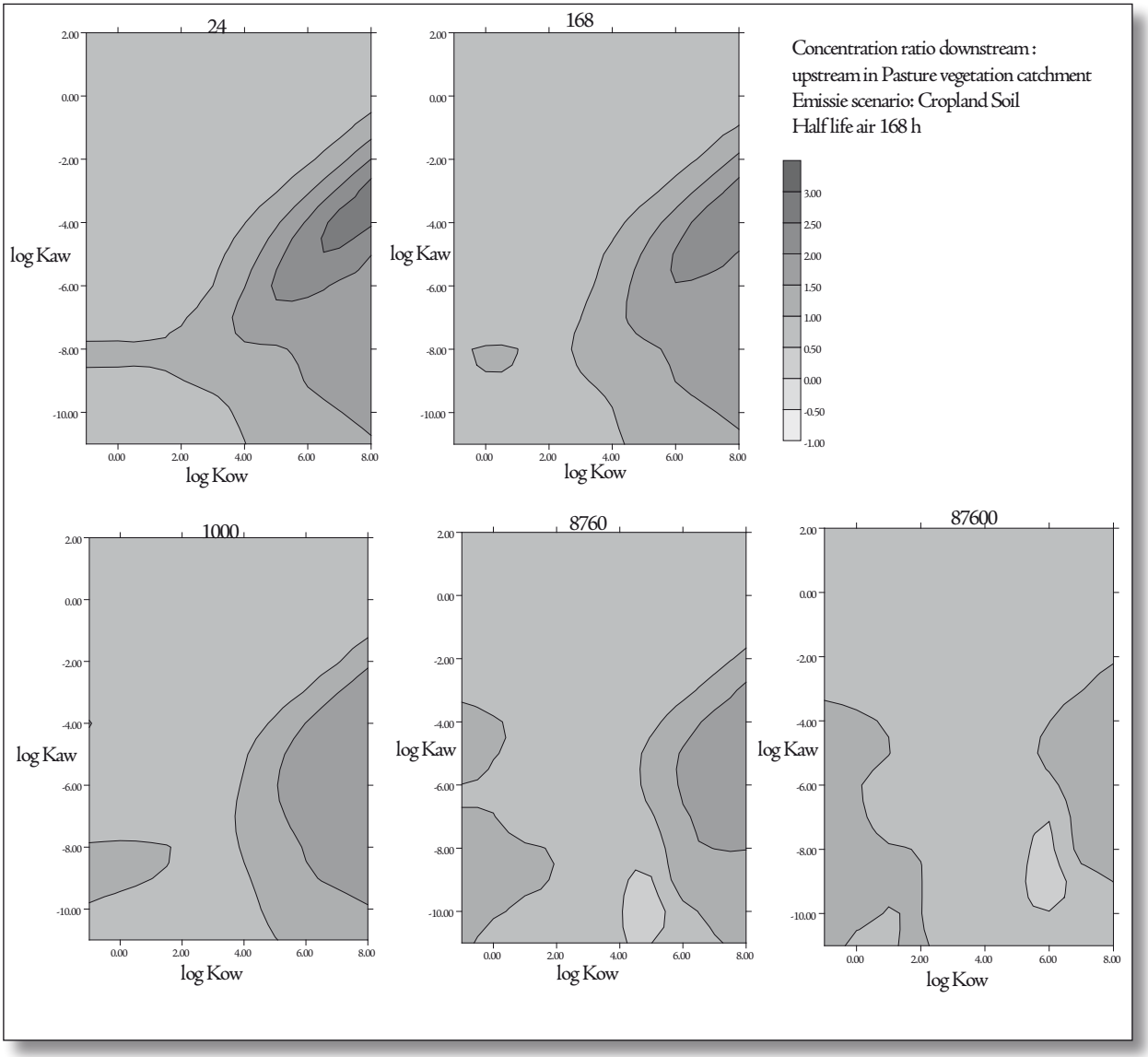
Appendix B6


24
168
1000
8760
87600
log Kaw
log Kow
Concentration ration downstream : upstream in Pasture soil catchment
Emission scenario: Cropland Soil
Half life air 168 h
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

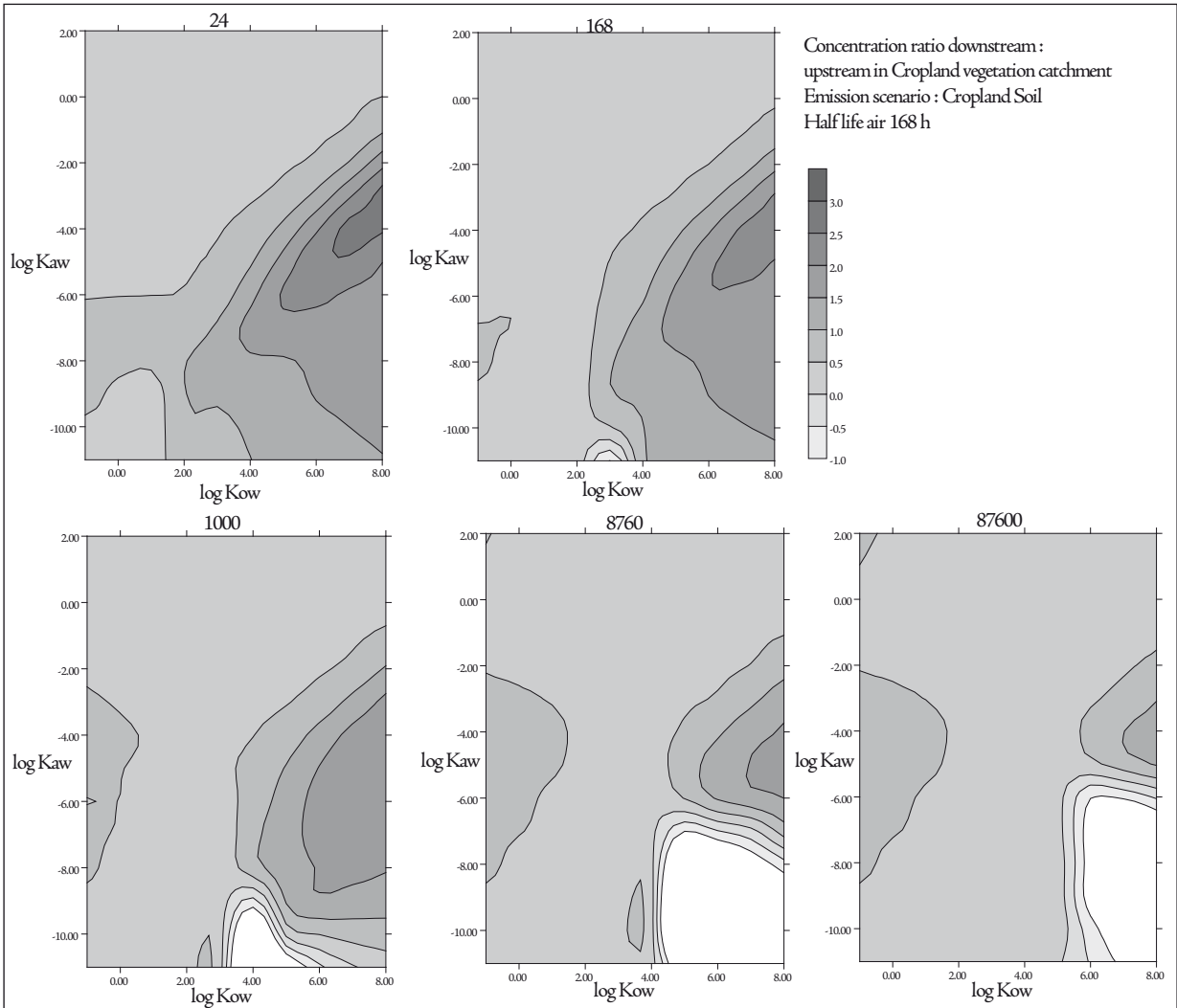
Appendix B7


24
168
1000
8760
87600
log Kaw
log Kow
Concentration ratio downstream : upstream in natural soils catchment
Emission scenario: Cropland Soil
Half life air = 168 h
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

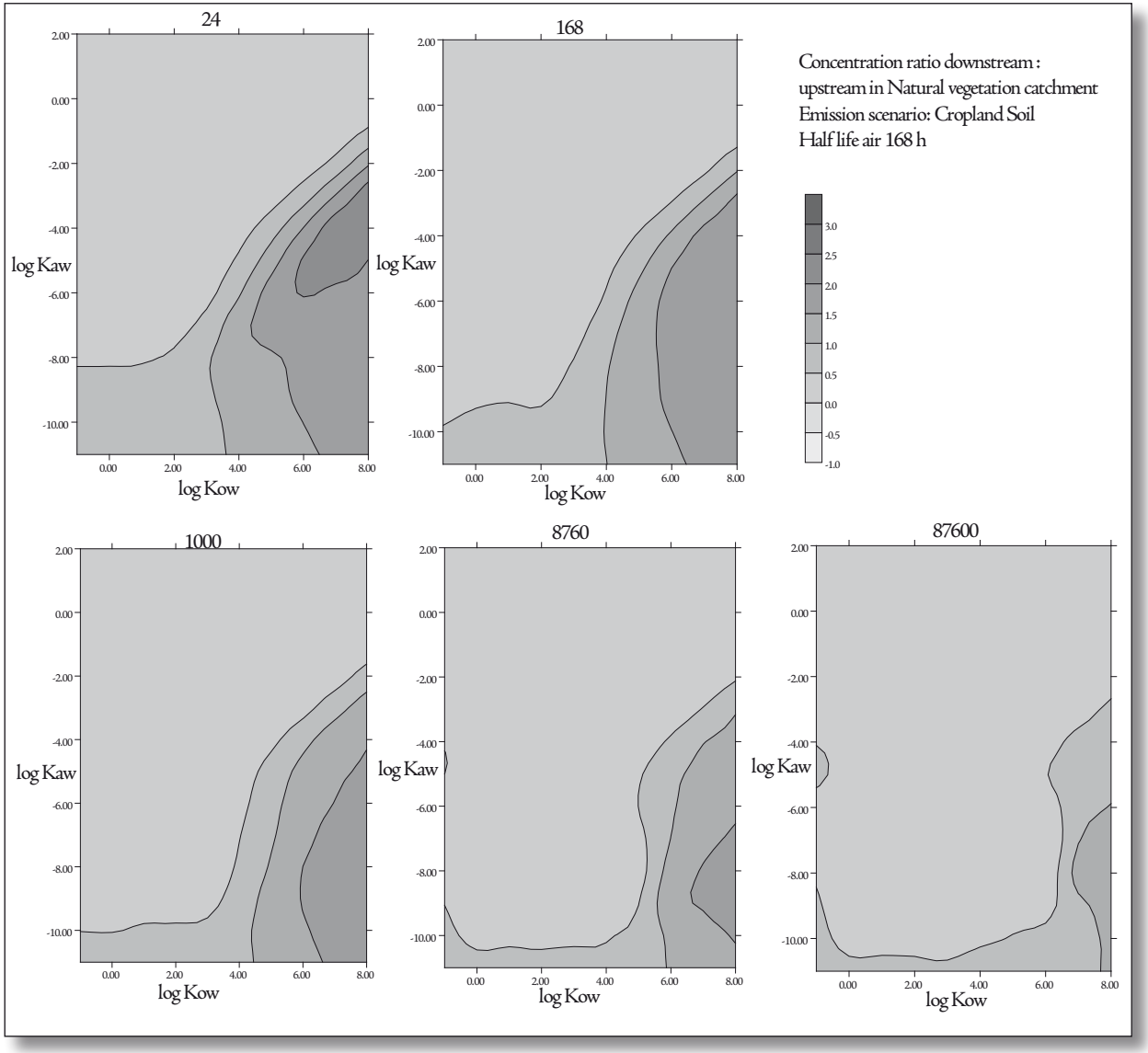
Appendix B8


24
168
1000
8760
87600
log Kaw
log Kow
Concentration ratio downstream : upstream in Pasture vegetation catchment
Emissie scenario: Cropland Soil
Half life air 168 h
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00

Appendix B9



Appendix B10



Appendix B11

Appendix C: Supporting information 'Spatial variance in multimedia mass balance models: comparison of LOTOS-EUROS and SimpleBox for PCB-153'

Appendix C1 Measured concentrations of PCB-153 in Europe during the calculation period

Compartment	Year	Type of value(1)	Concentration	Unit	Reference
Soil	1990	min	$1.0*10^{+3}$(2)	$\mu g.m^{-3}$	Schwartz, 2000
Soil	1990	max	$1.1*10^{+5}$(2)	$\mu g.m^{-3}$	Schwartz, 2000
Soil	1990	average	$2.2*10^{+3}$(2)	$\mu g.m^{-3}$	Schwartz, 2000
Soil	1993	average	$5.4*10^{+2}$(2)	$\mu g.m^{-3}$	Cousins and Jones, 1998
Soil	1998	min	$1.7*10^{+1}$	$\mu g.m^{-3}$	Meijer et al., 2003
Soil	1998	max	$1.1*10^{+3}$	$\mu g.m^{-3}$	Meijer et al., 2003
Soil	1998	average	$3.9*10^{+2}$	$\mu g.m^{-3}$	Meijer et al., 2003
Air	1991	point value	$1.4*10^{-5}$	$\mu g.m^{-3}$	Coleman et al., 1998
Air	1992	point value	$1.2*10^{-5}$	$\mu g.m^{-3}$	Coleman et al., 1998
Air	1992	point value	$5.1*10^{-5}$	$\mu g.m^{-3}$	Berg et al., 1996
Air	1992	point value	$1.5*10^{-6}$	$\mu g.m^{-3}$	Oehme et al., 1995
Air	1992	point value	$9.9*10^{-7}$	$\mu g.m^{-3}$	Oehme et al., 1995
Air	1992	point value	$9.9*10^{-7}$	$\mu g.m^{-3}$	Oehme et al., 1995
Air	1992	point value	$1.1*10^{-5}$	$\mu g.m^{-3}$	Kaupp et al., 1996
Air	1993	average	$1.9*10^{-6}$	$\mu g.m^{-3}$	Cousins and Jones, 1998
Air	1993	point value	$3.2*10^{-5}$	$\mu g.m^{-3}$	Berg et al., 1996
Air	1993	point value	$6.1*10^{-7}$	$\mu g.m^{-3}$	Berg et al., 1996
Air	1993	point value	$6.0*10^{-6}$	$\mu g.m^{-3}$	Coleman et al., 1998
Air	1994	point value	$2.8*10^{-5}$	$\mu g.m^{-3}$	Berg et al., 1996
Air	1994	point value	$6.2*10^{-7}$	$\mu g.m^{-3}$	Berg et al., 1996
Air	1994	point value	$5.8*10^{-6}$	$\mu g.m^{-3}$	Berg and Hjellbrekke, 1998
Air	1994	point value	$4.0*10^{-5}$	$\mu g.m^{-3}$	Coleman et al., 1998
Air	1995	min	$7.0*10^{-6}$	$\mu g.m^{-3}$	Schwartz, 2000
Air	1995	max	$1.3*10^{-4}$	$\mu g.m^{-3}$	Schwartz, 2000
Air	1995	average	$4.3*10^{-5}$	$\mu g.m^{-3}$	Schwartz, 2000
Air	1995	point value	$3.9*10^{-5}$	$\mu g.m^{-3}$	Berg et al., 1996
Air	1995	point value	$3.2*10^{-7}$	$\mu g.m^{-3}$	Berg et al., 1996
Air	1995	point value	$4.4*10^{-6}$	$\mu g.m^{-3}$	Brorstrom-Lunden et al., 2000
Air	1995	point value	$2.2*10^{-5}$	$\mu g.m^{-3}$	Coleman et al., 1998
Air	1996	point value	$2.2*10^{-6}$	$\mu g.m^{-3}$	Berg and Hjellbrekke, 1998

Compartment	Year	Type of value(1)	Concentration	Unit	Reference
Air	1996	point value	$2.1*10^{-6}$	$\mu g.m^{-3}$	Brorstrom-Lunden et al., 2000
Air	1996	point value	$1.5*10^{-6}$	$\mu g.m^{-3}$	Brorstrom-Lunden et al., 2000
Air	1996	point value	$1.3*10^{-5}$	$\mu g.m^{-3}$	Coleman et al., 1998
Air	1996	point value	$9.8*10^{-6}$	$\mu g.m^{-3}$	Vana et al., 2001
Air	1997	point value	$4.1*10^{-5}$	$\mu g.m^{-3}$	Berg and Hjellbrekke, 1999
Air	1997	point value	$7.0*10^{-7}$	$\mu g.m^{-3}$	Berg and Hjellbrekke, 1999
Air	1997	point value	$1.5*10^{-6}$	$\mu g.m^{-3}$	Brorstrom-Lunden et al., 2000
Air	1997	point value	$3.1*10^{-7}$	$\mu g.m^{-3}$	Brorstrom-Lunden et al., 2000
Air	1997	point value	$1.7*10^{-6}$	$\mu g.m^{-3}$	Coleman et al., 1998
Air	1998	point value	$1.6*10^{-6}$	$\mu g.m^{-3}$	Brorstrom-Lunden et al., 2000
Air	1998	point value	$4.9*10^{-7}$	$\mu g.m^{-3}$	Brorstrom-Lunden et al., 2000
Air	1998	point value	$4.6*10^{-5}$	$\mu g.m^{-3}$	Vana et al., 2001
Air	1998	point value	$1.3*10^{-6}$	$\mu g.m^{-3}$	Berg et al., 2000
Air	1999	point value	$1.2*10^{-5}$	$\mu g.m^{-3}$	Berg et al., 2001
Air	1999	point value	$1.2*10^{-6}$	$\mu g.m^{-3}$	Berg et al., 2001
Air	1999	point value	$7.3*10^{-7}$	$\mu g.m^{-3}$	Kouimtzis et al., 2002
Air	2000	point value	$2.1*10^{-5}$	$\mu g.m^{-3}$	Berg et al., 2002
Air	2000	point value	$4.0*10^{-7}$	$\mu g.m^{-3}$	Berg et al., 2002
Air	2000	point value	$1.7*10^{-6}$	$\mu g.m^{-3}$	Berg et al., 2002
Air	2000	point value	$1.2*10^{-6}$	$\mu g.m^{-3}$	Berg et al., 2002
Air	2000	point value	$6.3*10^{-6}$	$\mu g.m^{-3}$	Mandalakis et al., 2002
Air	2000	point value	$2.1*10^{-6}$	$\mu g.m^{-3}$	Mandalakis et al., 2002

(1) In literature minimum (min), maximum (max), and average concentrations (average) as well as single point concentration values (point value) were recorded

(2) A soil density of 1600 $kg.m^{-3}$ is assumed to convert the concentrations from $g.kg^{-1}$ to $\mu g.m^{-3}$

Appendix C1. Measured concentrations of PCB-153 in Europe during the calculation period.

References Appendix C

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Appendix D: Supporting information 'Estimating overall persistence and long-range transport potential of persistent organic pollutants: seven multimedia mass balance models and atmospheric transport models in comparison'

Appendix D1: Physical-chemical properties and degradation rate constants of the 14 chemicals selected for the P_{ov} and LRTP rankings

Appendix D2: Description of the seven models

Appendix D3: Statistics of P_{ov} and LRTP rankings of the 14 reference chemicals

Appendix D4: Mass balance estimates for PCB-153 in the year 2000

Chemical	Vapor pressure Pa (25°C)	Solubility mol.m^{-3} (25°C)	K_{aw} –	K_{ow} –	k_{air} s^{-1}	k_{soil} s^{-1}	k_{water} s^{-1}	k_{sed} s^{-1}	k_{veg} s^{-1}
aldrin	6.37E-2a	2.63E-3a	9.77E-3a	1.78E+6a	6.64E-5o	5.03E-8o,e	7.20E-8o	7.20E-9o	6.64E-5v
atrazine	3.87E-5b	1.42E-1b	1.10E-7b	5.62E+2b	3.11E-5h	2.36E-7p	2.33E-7h	1.91E-8h	3.11E-5v
B[a]P	6.32E-6a	1.14E-4a	2.24E-5a	8.92E+5a	3.63E-5u,j	1.13E-8q	1.13E-7q	3.50E-9u	3.63E-5v
BDE-47	2.15E-4c	1.94E-4c	4.46E-4c	2.43E+6c	7.52E-7k	9.63E-9k	9.63E-9k	9.63E-10k	7.52E-7v
BDE-99	3.63E-5c	6.86E-5c	2.14E-4c	5.72E+6c	4.12E-7k	9.63E-9k	9.63E-9k	9.63E-10k	4.12E-7v
biphenyl	4.21a	1.66E-1a	1.05E-2a	1.10E+4a	4.86E-6l	3.50E-7r	1.13E-6r	1.13E-7l	4.86E-6v
CCl4	1.65E+4d	4.64d	1.44f	6.76E+2d	2.90E-10m	3.15E-8o	3.15E-8o	1.60E-7m	2.90E-10v
HCB	1.01E-1a	1.32E-3a	3.09E-2a	4.07E+5a	1.96E-8n	5.64E-9o	5.64E-9o	5.64E-10n	1.96E-8v
HCBD	1.78E+1d	1.28E-2d	5.59E-1d	2.42E+4d	1.62E-8u,j	4.58E-8d,s	8.02E-8t	8.02E-9u	1.62E-8v
PCB-153	5.51E-4a	3.02E-5a	7.41E-3a	7.24E+6a	1.16E-7j	3.50E-10j	3.50E-9j	1.13E-9j	1.16E-7v
PCB-180	1.32E-4a	1.70E-5a	3.09E-3a	1.41E+7a	7.25E-8j	1.93E-10j	3.50E-9j	1.13E-9j	7.25E-8v
PCB-28	2.58E-2a	8.91E-4a	1.17E-2a	4.57E+5a	7.55E-7j	1.93E-8j	3.50E-8j	1.13E-8j	7.55E-7v
p-cresol	1.51E+1e	1.10E+2e	5.51E-5e	9.33E+1e	3.21E-5e	4.81E-5e	3.57E-5e	3.57E-6e	3.21E-5v
α-HCH	2.26E-1a	3.55E-1a	2.57E-4a	7.59E+3a	1.02E-7n	5.94E-8o	5.94E-8o	3.50E-9n	1.02E-7v

a = Schenker et al., 2005, b = US EPA, 2005, c = Wania and Dugani, 2003, d = Mackay et al., 1992, e = Mackay et al., 1999, f = Hunter-Smith et al., 1983, h = Fenner et al,. 2003, j = Wania and Daly, 2002, k = Gouin and Harner, 2003, l = Anderson and Hites, 1996, m = Atkinson et al., 1989, n = Brubaker and Hites, 1998, o = Howard, 1991, p = Lanz, 2005, q = Mackay et al., 1992a, r = Mackay et al, 1992b, s = Eisenberg and McKone, 1998, t = HSDB, 2001, u = Howard and Meylan, 1997, v = degradation rate constants in vegetation assumed equal to those of air

Appendix D1: Physical-chemical properties and degradation rate constants of the 14 chemicals selected for the P_{ov} and LRTP rankings.

Appendix D2: Description of the seven models

EVn-BETR

The European Variant Berkeley–Trent model (EVn-BETR) is a fugacity-based model (Mackay, 2001) that comprises 50 regions, with 4 regions in the periphery to describe the outside Europe world. Each region represents an area of approximately 500x500 km (5°x5°), with the whole model domain covering an area from 38.7°N to 61.1°N latitude and 10.1°W to 39.4°E longitude (Prevedouros et al., 2004). Each region consists of seven environmental compartments: lower (0–1000 m) and upper air (1000–2000 m), soil, vegetation, ocean water, fresh water and sediment. Detailed information on the model construction can be found in MacLeod et al. (2001) and Woodfine et al. (2001).

MSCE-POP

MSCE-POP is a multi-compartment atmospheric transport model, describing processes in and exchange between four environmental compartments (atmosphere, soil, sea water, and vegetation). Except the vegetation compartment, all compartments are vertically segmented into a number of layers. There are regional and hemispherical versions of the model. The spatial resolution of the latter version, which was used in the EMEP POP model inter-comparison study, is 2.5 x2.5° and the model domain covers the total Northern Hemisphere. Lateral transport of compounds by air and by seawater is taken into account in the model. (Malanichev et al., 2004, Gusev et al., 2005).

ClimoChem

ClimoChem is a multi-compartment mass balance box model that covers the entire global system. Compartments included are soil, oceanic surface water, troposphere air, vegetation and vegetation soil. ClimoChem is a two-dimensional model containing a flexible number of (typically 10 to 30) latitudinal zones with different temperatures and compartment volumes. ClimoChem does not have a spatial resolution in the East-West direction; in North-South direction, the spatial resolution is given by the number of zones, n, and the width of a zone is equal to 180/n degrees latitude (Scheringer et al., 2000).

SimpleBox

SimpleBox is a nested level III and level IV 'Mackay type' multimedia fate model consisting of ten environmental compartments on local, regional, continental and global scales (Brandes et al., 1996; Den Hollander et al., 2004). The regional and continental scales distinguish an air compartment (atmospheric mixing layer), a sea water compartment with a sediment compartment, a fresh water compartment with a sediment compartment, and three types of soil compartments (natural, agricultural, other soil) with corresponding vegetation compartments. SimpleBox is a generic model, in which the default settings are set to match the European Union procedures for the evaluation of substances (Brandes et al., 1996).

ADEPT

ADEPT (Atmospheric DEPosition and Transport model for risk assessment) is a diagnostic model that calculates concentrations in air and deposition fluxes

to the underlying surface; Roemer et al., 2004). The model is derived from the LOTOS-EUROS model (Schaap et al., 2005). It covers the European continent (30°N-70°N; and 10°W to 60°E), but it can be adjusted to sub-domains. There is no exchange with water, soil and vegetation, only a flux (loss term) to the underlying surface. Transport characteristics are taken from the LOTOS-EUROS model by means of source receptor matrices for inert species. Loss by chemistry, wet and dry deposition is modeled on the basis of the average transport time from source to receptor, and by means of average values for OH, O3, photolysis, atmospheric and surface resistances, precipitation and Henry coefficients.

G-CIEMS

G-CIEMS is a GIS-based geo-referenced multimedia fate model consisting of environmental compartments of gridded air cells, polygon and line-based surface catchments and river structures, and polygon-based sea segments (Suzuki et al., 2005). The model is now mainly applied to the Japan-regional environment with detailed (ca. 5 km) resolutions. As the model is flexible to any geographical conditions within the computational limitations, a generic simple framework consisting of only several boxes including the specified European modeling domain and surrounding areas was used in this study, so that essential comparison of the multimedia fate processes would be possible.

model	average deviation of all 14 chemicals	chemical	average deviation of all 6 models
CliMoChem	0.428	p-cresol	0.333
MSCE-POP	0.428	CCl4	0.333
G-CIEMS	0.428	a-HCH	0.50
OECD Tool	0.571	BDE-47	0.50
SimpleBox	1.0	aldrin	0.667
EVN-BETR	1.29	biphenyl	0.667
		BDE-99	0.667
		HCB	0.667
		PCB-180	0.667
		atrazine	0.833
		BaP	0.833
		PCB-28	0.833
		PCB-153	0.833
		HCBD	1.33
		average of all 14 chemicals	0.69

Table 1: average deviations of P_{ov} rankings from average ranking of the 14 chemicals: average over all 14 chemicals in each of the 6 models (left) and average over the 6 models for each chemical (right).

model	average deviation of all 14 chemicals	chemical	average deviation of all 8 models
OECD Tool (CTD)	0.714	p-cresol	0.375
OECD Tool (TE)	1.0	aldrin	0.5
G-CIEMS	1.29	BaP	0.625
MSCE-POP	1.29	BDE-47	1.125
SimpleBox	1.29	HCB	1.375
EVN-BETR	1.43	CCl4	1.375
ADEPT	2.0	PCB-153	1.375
CliMoChem	2.43	HCBD	1.5
		biphenyl	1.75
		atrazine	1.75
		a-HCH	1.875
		PCB-28	1.875
		PCB-180	2.25
		BDE-99	2.25
		average of all 14 chemicals	1.43

Table 2: average deviations of LRTP rankings from average ranking of the 14 chemicals: average over all 14 chemicals in each of the 8 models (left) and average over the 8 models for each chemical (right).

Appendix D3: Statistics of P_{ov} and LRTP rankings of the 14 reference chemicals.

	MSC-E POP		*CliMoChem*		*SimpleBox*		*EVn-BETR*		*G-CIEMS*	
Volume										
air (m^3)	*1,26E+17*		*6,19E+16*		*9,59E+15*		*1,06E+16*		*1,05E+17*	
water (m^3)	*9,83E+14*		*8,41E+14*		*8,68E+14*		*4,25E+14*		*9,84E+14*	
sediment (m^3)	*na*				*1,35E+11*		*3,81E+09*		*2,18E+11*	
soil (m^3)	*1,11E+12*		*5,92E+11*		*6,11E+11*		*5,58E+11*		*5,57E+11*	
vegetation (m^3)	*nr*		*5,00E+09*		*8,34E+09*		*3,26E+09*		*6,25E+08*	
Concentration 2000										
air (pg/m^3)			*0,44*		*3,7*		*7,5*		*4,9*	
interface with ocean	*3,7*									
interface with soil	*7,4*									
interface with vegetation	*7,4*									
water (pg/L)			*0,21*		*2,0*		*1,70*		*0,2*	
interface with atmosphere	*0,18*									
sediment (pg/g)	*na*		*na*		*107*		*73,0*		*2*	
soil (pg/g)			*12,07*		*40*		*26,0*		*63*	
interface with atmosphere	*168*									
vegetation (pg/g)	*2634*		*16,24*		*18*		*105*		*1363*	
Mass 2000										
air (kg)	*107*	*0,1%*	*27*	*0,1%*	*38*	*0,1%*	*79*	*0,2%*	*61*	*0,1%*
water (kg)	*1285*	*1,4%*	*180*	*1,0%*	*1759*	*3,6%*	*722,9*	*2,0%*	*171*	*0,4%*
sediment (kg)	*na*				*20187*		*667,5*	*1,8%*	*717*	*1,7%*
soil (kg)	*84167*	*95%*	*17860*	*97,8%*	*46687*	*96%*	*34804*	*95,1%*	*41809*	*99%*
forest litter (kg)	*2709*							*0,0%*		
vegetation (kg)	*684*	*0,8%*	*203*	*1,1%*	*161*	*0,3%*	*342*	*0,9%*	*42*	*0,1%*
total mass (kg)	*88952*	*100%*	*18270*	*100,0%*	*48645*	*100%*	*36616*	*100,0%*	*42082*	*100%*
Changes in inventory from 1999 to 2000										
air (kg/yr)	*4,4*	*4,1%*	*-2,28*	*-8%*	*-2,8*	*-7,5%*	*-7*	*-8,8%*	*-29,7*	*-48,9%*
water (kg/yr)	*-78*	*-6,1%*	*-12,60*	*-7%*	*-158*	*-9,0%*	*-62*	*-8,6%*	*-108*	*-63,2%*

	MSC-E POP		CliMoChem		SimpleBox		EVn-BETR		G-CIEMS	
sediment (kg/yr)					-1862	-9,2%	-22		642	89,6%
soil (kg/yr)	-3782	-4,5%	-412	-2%	-3251	-7,0%	-550	-1,6%	-3390	-8,1%
forest litter (kg/yr)	-188	-7,0%								
vegetation (kg/yr)	-25	-3,6%	-18	-9%	-13	-8,2%	-27	-7,9%	-46	-112,0%
total (kg/yr)	-4069		-445		-5288		-668		-2932	
Mass balances for individual media										
air (kg/yr)	-35	-32,7%	1	2,9%	-9	-24,3%	10,0	12,6%	-187	-308,7%
water (kg/yr)	-46	-3,6%	0	-0,3%	51	2,9%	-4,0	-0,6%	-248	-144,5%
sediment (kg/yr)					101	0,5%	94,0	14,1%	582	81,2%
soil (kg/yr)	381	0,5%	-35	-0,2%	-997	-2,1%	-501,0	-1,4%	-4206	-10,1%
forest litter (kg/yr)	-381	-14,1%								
vegetation (kg/yr)	0	0,0%	5	2,3%	-9	-5,6%	365,0	106,6%	-90	-216,9%
total (kg/yr)	-80	-0,1%	-30	-0,2%	-864	-1,8%	-36,0	-0,1%	-4149	-9,9%
Mass budget										
emission to model domain (kg/yr)	5546	100%	995	100%	5535	100%	7568	100%	5452	100%
emission to rest of N hemishere (kg/yr)	5844								5446	
net export from domain with air (kg/yr)	3474	63%	208	21%	676	12%	2797	37%	2832	52%
net export from domain with water (kg/yr)	-17,2	-0,3%	8,2	0,8%	1251	23%	3041,00	40%	412	7,6%
reaction in air (kg/yr)	45	0,8%	12	1,2%	41,7	0,8%	87,0	1,1%	89,8	1,6%
reaction in water (kg/yr)	33	0,6%	9,2	0,9%	447	8,1%	81,00	1,1%	54	1,0%
reaction in sediment (kg/yr)					2276	41%	43,00	0,6%	54	1,0%
reaction in soil (kg/yr)	4343	78%	844	85%	5238	95%	1861,00	25%	4897	90%
reaction in litter layer (kg/yr)	569	10%								
reaction in vegetation (kg/yr)	0	0%	101	10%	180	3,2%	110,0	1,5%	161	3,0%

	MSC-E POP		*CliMoChem*		*SimpleBox*		*EVn-BETR*		*G-CIEMS*	
burial in sediment (kg/yr)					*75*	*1,4%*			*0,04*	*0,0%*
leaching from soil (kg/yr)					*0,44*	*0,0%*			*0,00*	*0,0%*
removal of plants (kg/yr)					*112*	*2,0%*			*0*	*0,0%*
deposition to deep sea (kg/yr)	*1213*	*22%*	*289*	*29%*						
removal from model domain (kg/yr)	*9660*	*174%*	*1471*	*148%*	*10298*	*186%*	*8020,00*	*106%*	*8501*	*156%*
Intermedia flow										
dry deposition to water (kg/yr)	*58*				*327*				*304*	
wet deposition to water (kg/yr)	*461*				*1457*				*525*	
gas absorption to water (kg/yr)	*620*				*378*				*560*	
total deposition to water	*1140*	*21%*	*258*	*26%*	*2162*	*39%*	*3171*	*42%*	*1389*	*25%*
dry deposition to soil (kg/yr)	*1006*				*355*				*189*	
wet deposition to soil (kg/yr)	*1530*				*1647*				*326*	
gas absorption to soil (kg/yr)	*-2864*				*213*				*1*	
total deposition to soil	*-329*	*-5,9%*	*215*	*22%*	*2215*	*40%*	*810*	*11%*	*517*	*9,5%*
dry deposition to vegetation (kg/yr)	*246*				*28*				*156*	
wet deposition to vegetation (kg/yr)	*0*				*40*				*270*	
gas absorption to vegetation (kg/yr)	*1001*				*384*				*416*	
total deposition to vegetation	*1247*	*22%*	*304*	*31%*	*453*	*8,2%*	*700*	*9,2%*	*841*	*15%*
total atmospheric deposition	*2057*	*37%*	*777*	*78%*	*4830*	*87%*	*4681*	*62%*	*2747*	*50%*
sedimentation (kg/yr)					*590*	*11%*	*115,000*	*1,5%*	*1279*	*23%*
run off to surface water (kg/yr)			*35*	*3,55%*	*18*	*0,3%*				*0,0%*
litter fall to soil (kg/yr)	*1271*	*23%*	*217*	*22%*	*183*	*3,3%*	*252,0*	*3,3%*	*817*	*15,0%*

Appendix D4: Mass balance estimates for PCB-153 in the year 2000.

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Appendix E: Supporting information 'Substance or space? The relative influence of substance properties and landscape characteristics in modeling the fate of chemicals in Europe'

Appendix E1: Physical-chemical input data for the 200 compounds used in this study

Appendix E2: Frequency distributions of the environmental input data

Appendix E3: Environmental input parameter values for each of the 137 regions on a 250x250 km scale

Appendix E4a: Correlation matrix of the environmental and chemical input parameters

Appendix E4b: Data transformation for stepwise multiple regression analysis

Appendix E5: Average concentration ranges on the 250x250, 100x100 and 50x50 km scales

	CAS	Name	g/mol MW	oC Tmelt	Pa VP 25o	mg/L S 25o	- K_{OW}	s-1 kdeg(air)25o	s-1 kwater	s-1 ksed	s-1ksoil
1	60-57-1	Dieldrin	3,8E+02	1,8E+02	5,0E-04	1,7E-01	1,6E+05	7,9E-06	1,8E-08	2,7E-06	1,8E-08
2	18691-97-9	Methabenzthiazuron	2,2E+02	1,2E+02	1,5E-05	6,3E+01	2,0E+02	1,6E-05	8,9E-08	1,9E-08	5,9E-08
3	1746-01-6	2,3,7,8-TCDD	3,2E+02	3,1E+02	2,0E-07	2,5E-05	8,1E+06	4,3E-07	4,1E-06	4,4E-09	1,3E-08
4	1330-20-7	Xylenes (total)	1,1E+02	-2,5E+01	1,1E+03	1,9E+02	1,3E+03	7,3E-06	5,7E-07	8,6E-08	5,7E-07
5	110-54-3	HEXANE	8,6E+01	-9,5E+01	2,0E+04	9,5E+00	1,3E+04	1,1E-05	3,5E-07	4,3E-08	1,1E-07
6	16752-77-5	Methomyl	1,6E+02	7,9E+01	6,7E-03	5,8E+04	4,0E+00	8,0E-06	6,6E-08	1,5E-07	4,1E-07
7	2921-88-2	Chlorpyriphos	3,5E+02	4,2E+01	2,3E-03	7,3E-01	8,3E+04	3,0E-05	5,3E-07	2,8E-07	3,9E-07
8	85-68-7	Butylbenzylphtalate	3,1E+02	-3,5E+01	8,6E-04	2,7E+00	5,6E+04	5,3E-06	3,0E-06	4,0E-07	3,0E-06
9	50-29-3	DDT	3,5E+02	1,1E+02	2,0E-05	5,5E-03	1,5E+06	1,8E-06	1,7E-07	1,8E-07	3,9E-09
10	106-46-7	1,4-dichlorobenzene	1,5E+02	5,3E+01	1,5E+02	7,2E+01	2,9E+03	1,6E-07	1,1E-07	3,7E-08	1,8E-08
11	309-00-2	Aldrin	3,6E+02	1,0E+02	5,0E-03	2,0E-02	1,0E+03	3,5E-05	8,3E-08	2,7E-06	8,3E-08
12	no value	totaal-PAK (carcinogenic)	2,4E+02	2,0E+02	2,5E-04	5,9E-02	1,1E+06	3,2E-05	1,1E-08	3,6E-09	1,1E-08
13	2303-17-5	Tri-allaat	3,0E+02	3,0E+01	1,5E-02	4,0E+00	1,9E+04	1,6E-05	1,3E-07	3,7E-07	1,1E-06
14	86-73-7	Fluorene	1,7E+02	1,2E+02	8,5E-02	1,9E+00	1,5E+04	4,7E-06	1,8E-07	6,0E-08	1,8E-07
15	11097-69-1	PCB-1254	3,4E+02	1,0E+02	1,0E-03	5,5E-02	2,6E+06	1,2E-07	2,9E-08	1,4E-09	8,5E-09
16	75-00-3	CHLOROETHANE	6,4E+01	-1,4E+02	1,3E+05	5,7E+03	2,7E+01	2,0E-07	7,8E-07	4,0E-07	7,8E-07
17	70648-26-9	HEXACHLORINATED DIBENZOFURAN, 1,2,3,4,7,8-	3,7E+02	2,3E+02	3,1E-06	8,2E-06	1,0E+07	1,0E-40	2,0E-08	7,9E-10	2,0E-09
18	75-68-3	1,1-DIFLUORO-1-CHLOROETHANE	1,0E+02	-1,3E+02	3,4E+05	1,4E+03	1,1E+02	2,6E-09	6,4E-05	6,4E-06	6,4E-05
19	41394-05-2	Metamitron	2,0E+02	1,7E+02	2,0E-06	1,8E+03	4,9E+00	1,8E-05	6,9E-07	3,5E-07	5,3E-07
20	51207-31-9	2,3,7,8-TETRACHLORODIBENZOFURAN	3,1E+02	2,3E+02	2,0E-04	4,2E-04	1,3E+06	1,1E-06	3,5E-07	4,3E-09	1,1E-08
21	74-83-9	Methylbromide = bromomethane	9,5E+01	-9,3E+01	1,7E+03	1,4E+04	1,5E+01	1,9E-08	1,2E-06	8,5E-07	1,2E-06
22	109-69-3	1-Chlorobutane	9,3E+01	-1,2E+02	1,4E+04	6,1E+02	4,4E+02	5,6E-06	5,7E-07	1,9E-07	5,7E-07
23	87-68-3	hexachloro-1,3-butadiene	2,6E+02	-2,1E+01	2,0E+01	3,2E+00	5,0E+04	1,1E-08	1,1E-07	3,7E-08	1,1E-07

	CAS	Name	g/mol MW	oC Tmelt	Pa VP 25o	mg/L S 25o	- K_{OW}	s-1 kdeg(air)25o	s-1 kwater	s-1 ksed	s-1ksoil
24	110-80-5	CELLOSOLVE	9,0E+01	-7,0E+01	7,1E+02	1,0E+06	4,8E-01	6,0E-06	5,7E-07	1,9E-07	5,7E-07
25	99308-24-4	C9-chloroether	3,2E+02	2,7E+01	1,9E-03	9,6E+00	4,0E+03	2,5E-06	6,6E-09	2,6E-10	2,0E-09
26	123-91-1	1,4-DIOXANE	8,8E+01	1,2E+01	5,1E+03	1,0E+06	5,4E-01	4,0E-06	1,3E-07	3,7E-08	1,1E-07
27	67-72-1	Hexachloroethane	2,4E+02	1,9E+02	6,7E+01	4,2E+01	1,0E+04	5,3E-10	1,1E-07	3,7E-08	1,1E-07
28	72-43-5	Methoxychlor	3,5E+02	9,3E+01	1,7E-04	1,1E-01	4,5E+04	2,9E-05	5,6E-05	1,0E-07	5,2E-08
29	14816-18-3	Phoxim	3,0E+02	6,1E+00	3,0E-03	1,6E+00	2,4E+03	4,9E-05	1,1E-06	1,1E-06	1,2E-06
30	10265-92-6	Methamydophos	1,4E+02	4,6E+01	4,7E-03	1,0E+06	1,6E-01	1,7E-05	5,0E-07	1,0E-06	3,1E-06
31	74-88-4	METHYL IODIDE	1,4E+02	-6,6E+01	5,4E+04	1,4E+04	3,2E+01	6,0E-08	8,8E-07	2,6E-07	6,5E-07
32	115-29-7	Endosulfan	4,1E+02	8,4E+01	1,3E-03	5,0E-01	4,0E+03	1,3E-05	2,5E-06	1,4E-06	1,6E-06
33	1698-60-8	Chloridazon	2,2E+02	2,1E+02	7,0E+00	3,6E+02	1,4E+01	2,4E-05	5,3E-08	8,7E-08	2,7E-07
34	634-66-2	1,2,3,4-tetrachloroben-zene	2,2E+02	4,8E+01	5,2E+00	7,8E+00	3,2E+04	4,2E-08	1,1E-07	3,6E-08	1,1E-07
35	193-39-5	Indeno[1,2,3-cd]pyrene	2,8E+02	1,6E+02	1,3E-08	6,2E-02	3,8E+06	5,1E-05	5,8E-08	3,9E-09	1,2E-08
36	138261-41-3	Imidacloprid	2,6E+02	1,4E+02	2,2E-04	6,1E+02	3,7E+00	7,6E-05	1,4E-07	1,4E-08	4,5E-08
37	88-72-2	2-nitrotoluene	1,4E+02	-3,7E+00	1,8E+01	6,5E+02	2,0E+02	1,1E-05	3,5E-06	4,3E-08	1,1E-07
38	57117-31-4	2,3,4,7,8-PEN-TACHLORODIBEN-ZOFURAN	3,4E+02	2,0E+02	1,7E-05	2,4E-04	3,2E+06	3,5E-07	3,5E-07	4,3E-09	1,1E-08
39	107-05-1	ALLYL CHLORIDE	7,7E+01	-1,3E+02	4,9E+04	3,4E+03	8,5E+01	1,1E-05	1,4E-06	1,0E-06	1,4E-06
40	117-81-7	Di(2-ethylhexyl)phtalate	3,9E+02	-4,7E+01	1,3E-05	3,0E-03	2,0E+06	1,1E-05	8,5E-07	1,3E-07	7,5E-07
41	120-12-7	Anthracene	1,8E+02	2,2E+02	1,0E-03	4,5E-02	3,5E+04	6,5E-06	1,9E-04	1,7E-08	5,3E-08
42	608-93-5	pentachlorobenzene	2,5E+02	8,6E+01	2,2E-01	6,5E-01	1,0E+05	3,0E-08	3,1E-08	1,0E-08	3,1E-08
43	117-84-0	Dioctylphtalate	3,9E+02	-2,5E+01	1,3E-05	5,0E-04	1,1E+08	7,2E-06	5,7E-07	8,5E-08	5,7E-07
44	79-20-9	methyl acetate	7,4E+01	-9,8E+01	2,9E+04	2,5E+05	1,7E+00	3,5E-06	3,5E-06	4,3E-07	1,1E-06
45	108-70-3	1,3,5-trichlorobenzene	1,8E+02	6,4E+01	3,2E+01	5,3E+00	1,3E+04	2,5E-07	1,1E-07	3,7E-08	1,1E-07
46	107-02-8	Acrolein	5,6E+01	-8,7E+01	3,7E+04	2,1E+05	9,8E-01	9,8E-06	5,7E-07	1,8E-07	5,7E-07
47	67-56-1	METHANOL	3,2E+01	-9,8E+01	1,6E+04	1,2E+06	1,7E-01	4,5E-07	3,0E-06	3,5E-06	3,0E-06
48	60-51-5	Dimethoate	2,3E+02	5,2E+01	1,0E-02	2,0E+04	6,3E+00	6,8E-05	3,6E-07	1,4E-07	4,3E-07
49	52918-63-5	Deltamethrin	5,1E+02	1,0E+02	1,0E-05	2,0E-03	4,0E+04	2,0E-05	2,7E-06	1,0E-08	3,2E-07

	CAS	Name	g/mol MW	oC Tmelt	Pa VP 25o	mg/L S 25o	- K_{OW}	s-1 kdeg(air)25o	s-1 kwater	s-1 ksed	s-1ksoil
50	78-93-3	METHYL ETHYL KETONE	7,2E+01	-8,7E+01	1,2E+04	2,4E+05	1,9E+00	5,0E-07	3,0E-06	9,9E-07	3,0E-06
51	101-77-9	4,4'-DIAMINO DITAN	2,0E+02	9,3E+01	2,7E-05	1,0E+03	3,9E+01	1,2E-04	3,4E-06	9,9E-07	3,0E-06
52	123-31-9	HYDROQUINONE	1,1E+02	1,7E+02	1,3E-01	7,2E+04	3,9E+00	1,2E-05	7,3E-05	9,9E-07	3,0E-06
53	301-12-2	Oxydemethon-methyl	2,5E+02	-2,0E+01	5,4E-03	2,5E+04	1,8E-01	5,3E-05	8,3E-07	5,4E-06	1,6E-05
54	108-31-6	MALEIC ANHYDRIDE	9,8E+01	5,3E+01	3,3E+01	7,9E+05	4,2E+01	1,1E-06	4,4E-02	4,4E-02	4,4E-02
55	99308-27-7	C12-chloroether	4,1E+02	9,5E+01	2,6E-04	1,8E+00	5,0E+03	4,5E-06	6,6E-09	2,6E-10	2,0E-09
56	60-34-4	METHYL HYDRZINE	4,6E+01	-5,2E+01	6,6E+03	1,0E+06	3,2E-02	8,7E-05	4,5E-07	1,5E-07	4,5E-07
57	76-44-8	Heptachlor	3,7E+02	9,6E+01	5,3E-02	5,6E-02	1,9E+05	3,3E-05	3,7E-06	3,5E-06	3,7E-06
58	84-66-2	Diethylphtalate	2,2E+02	-4,1E+01	8,2E-02	1,1E+03	2,7E+02	1,5E-06	6,2E-07	1,5E-07	6,2E-07
59	115-07-1	PROPYLENE (PROPENE)	4,2E+01	-1,9E+02	1,0E+06	2,0E+02	5,9E+01	2,3E-05	6,0E-07	1,9E-07	5,7E-07
60	95-94-3	1,2,4,5-tetrachlorobenzene	2,2E+02	1,4E+02	7,2E-01	1,3E+00	3,2E+04	4,2E-08	1,1E-07	3,6E-08	1,1E-07
61	95-50-1	1,2-dichlorobenzene	1,5E+02	-1,7E+01	2,0E+02	1,2E+02	2,5E+03	2,1E-07	1,1E-07	3,6E-08	1,8E-08
62	120-82-1	1,2,4-trichlorobenzene	1,8E+02	1,7E+01	6,1E+01	4,0E+01	1,3E+04	2,5E-07	1,1E-07	3,7E-08	1,1E-07
63	83-32-9	Acenaphthene	1,5E+02	9,5E+01	9,5E-01	4,2E+00	9,3E+03	3,7E-05	1,5E-05	7,4E-08	2,3E-07
64	121-75-5	Malathion	3,3E+02	2,9E+00	1,0E-03	1,5E+02	6,3E+02	3,3E-05	5,9E-07	1,8E-07	1,8E-06
65	116-06-3	Aldicarb	1,9E+02	1,0E+02	4,0E-03	6,0E+03	1,3E+01	3,4E-05	1,1E-07	5,9E-08	1,1E-07
66	63-25-2	Carbaryl	2,0E+02	1,4E+02	2,7E-05	1,2E+02	2,3E+02	4,3E-05	3,5E-06	9,0E-07	1,2E-06
67	71-36-3	Butanol	7,4E+01	-8,9E+01	6,7E+02	7,5E+04	7,0E+00	3,7E-06	3,0E-06	7,9E-07	3,0E-06
68	151-56-4	AZIRIDINE	4,3E+01	-7,8E+01	2,8E+04	1,0E+06	5,2E-01	3,1E-06	5,7E-07	1,9E-07	5,7E-07
69	96-09-3	STYRENE OXIDE	1,2E+02	-3,5E+01	4,0E+01	3,0E+03	4,1E+01	2,6E-06	1,2E-05	1,0E-05	2,3E-05
70	75-56-9	propylene oxide	5,8E+01	-1,1E+02	7,1E+04	4,8E+05	1,1E+00	2,6E-07	1,5E-06	1,1E-06	1,2E-06
71	67562-39-4	1,2,3,4,6,7,8-HEPTACHLORODIBENZOFURAN	4,1E+02	2,4E+02	5,7E-07	1,4E-06	2,5E+07	3,5E-07	1,1E-07	4,3E-09	1,1E-08

	CAS	Name	g/mol MW	oC Tmelt	Pa VP 250	mg/L S 250	- K_{OW}	s-1 kdeg(air)250	s-1 kwater	s-1 ksed	s-1ksoil
72	1918-16-7	Propachlor	2,1E+02	7,1E+01	3,0E-02	6,0E+02	1,5E+02	1,1E-05	1,0E-06	4,3E-07	1,3E-06
73	77-78-1	DIMETHYL SULFATE	1,3E+02	-2,7E+01	9,1E+01	2,8E+04	1,4E+00	8,8E-07	1,6E-04	1,6E-04	1,6E-04
74	156-59-2	cis-1,2-Dichloroethylene	9,7E+01	-8,0E+01	2,4E+04	5,3E+03	5,2E+01	1,2E-06	7,7E-08	2,4E-08	5,1E-08
75	78-48-8	S,S,S-TRIBUTYLTRITHIOPHOSPHATE	3,1E+02	-2,5E+01	2,1E-01	1,6E+01	1,7E+03	2,7E-07	2,7E-08	1,1E-08	4,3E-06
76	95-80-7	2,4-DIAMINOTOLUENE	1,2E+02	9,9E+01	3,9E-02	3,0E+02	1,4E+00	1,2E-04	9,4E-07	3,7E-08	1,1E-07
77	30560-19-1	Acephate	1,8E+02	8,5E+01	2,3E-04	8,2E+05	1,0E-01	2,6E-05	1,5E-07	1,2E-06	3,6E-06
78	108-60-1	BIS(2-CHLORO-1-METHYLETHYL) ETHER	1,7E+02	-9,7E+01	1,2E+02	1,7E+03	3,0E+02	7,0E-06	1,4E-07	4,6E-08	1,4E-07
79	87-61-6	1,2,3-trichlorobenzene	1,8E+02	5,3E+01	2,8E+01	2,1E+01	1,3E+04	2,5E-07	1,1E-07	3,7E-08	1,1E-07
80	1634-04-4	METHYL TERT-BUTYL ETHER	8,8E+01	-1,1E+02	3,4E+04	5,1E+04	8,7E+00	1,2E-06	1,1E-07	3,7E-08	1,1E-07
81	76-13-1	CHLORINATED FLUOROCARBON (FREON 113)	1,9E+02	-3,5E+01	4,4E+04	1,7E+02	1,4E+03	3,6E-11	3,2E-08	1,0E-08	3,2E-08
82	206-44-0	Fluoranthene	2,0E+02	1,1E+02	1,2E-03	2,6E-01	1,7E+05	1,6E-05	5,3E-06	1,1E-08	3,2E-08
83	86-50-0	Azinphos-methyl	3,2E+02	7,4E+01	3,0E-05	3,0E+01	5,0E+02	1,5E-04	2,8E-06	2,2E-07	3,2E-07
84	639-58-7	Fentin chloride	3,9E+02	1,7E+02	1,0E+00	7,6E+01	1,3E+04	1,0E-40	1,1E-06	1,9E-09	5,7E-08
85	67129-08-2	Metazachlor	2,8E+02	8,5E+01	6,9E-05	4,6E+02	1,0E+02	3,4E-05	2,4E-07	1,4E-07	4,5E-07
86	110-00-9	Furan	6,8E+01	-8,5E+01	8,0E+04	1,0E+04	2,2E+01	6,8E-05	2,0E-06	1,9E-07	5,7E-07
87	108-88-3	Toluene	9,2E+01	-9,5E+01	3,8E+03	5,2E+02	4,9E+02	3,1E-06	1,2E-06	1,5E-07	8,6E-07
88	78-92-2	SEC-BUTYL ALCOHOL	7,4E+01	-1,1E+02	2,4E+03	1,8E+05	6,5E+00	4,5E-06	3,0E-06	9,9E-07	3,0E-06
89	57837-19-1	Metalaxyl	2,8E+02	7,2E+01	7,5E-04	8,4E+03	5,6E+01	1,3E-05	2,9E-07	3,7E-08	1,1E-07
90	84-74-2	Dibutylphtalate	2,8E+02	-3,5E+01	2,7E-03	1,1E+01	3,8E+04	4,3E-06	2,1E-06	1,2E-06	1,2E-06
91	118-96-7	2,4,6-trinitrotoluene	2,3E+02	8,0E+01	2,7E-04	1,2E+02	4,0E+01	7,3E-08	4,2E-04	1,1E-07	1,1E-07

	CAS	Name	g/mol MW	oC Tmelt	Pa VP 25o	mg/L S 25o	- K_{OW}	s-1 kdeg(air)25o	s-1 kwater	s-1 ksed	s-1ksoil
92	12674-11-2	Aroclor 1016	2,6E+02	6,5E+01	4,0E-01	1,4E-01	3,3E+05	1,8E-06	2,1E-07	6,3E-06	1,9E-05
93	72-20-8	Endrin	3,8E+02	2,1E+02	2,0E-05	2,3E-01	1,6E+05	1,3E-04	2,9E-09	8,6E-07	2,9E-09
94	74-90-8	HYDROCYANIC ACID	2,7E+01	-1,3E+01	9,9E+04	1,0E+06	5,6E-01	1,5E-08	1,2E-07	3,8E-08	1,2E-07
95	76-87-9	Fentin hydroxide	3,7E+02	1,2E+02	9,9E-06	1,1E+00	1,9E+03	1,0E-40	1,1E-06	1,9E-09	5,7E-08
96	634-90-2	1,2,3,5-tetrachlorobenzene	2,2E+02	5,5E+01	9,8E+00	3,6E+00	3,2E+04	4,2E-08	1,1E-07	3,6E-08	1,1E-07
97	100-25-4	1,4-dinitrobenzene	1,7E+02	1,7E+02	3,9E+02	1,3E+04	2,3E+02	3,2E-08	2,1E-07	7,0E-08	2,1E-07
98	79-46-9	2-NITROPROPANE	1,1E+02	-9,1E+01	2,4E+03	1,7E+04	8,5E+00	6,6E-06	1,1E-07	3,7E-08	1,1E-07
99	57-74-9	Chlordane	4,1E+02	1,0E+02	5,2E-04	5,6E-02	1,0E+06	6,2E-06	1,3E-08	2,7E-06	1,3E-08
100	630-20-6	1,1,1,2-TETRACHLORROETHANE	1,7E+02	-7,0E+01	1,6E+03	1,1E+03	8,5E+02	1,4E-08	2,3E-07	1,6E-07	1,3E-07
101	57018-04-9	Tolclophos-methyl	3,0E+02	7,9E+01	5,7E-02	3,0E-01	3,6E+04	3,1E-05	2,6E-07	4,0E-08	1,2E-07
102	999-81-5	chlormequat-chloride	1,6E+02	2,4E+02	1,4E-05	1,0E+06	1,6E-04	6,6E-07	2,9E-07	4,9E-07	1,5E-06
103	111-44-4	Bis(2-chloroethyl)ether	1,4E+02	-4,7E+01	1,8E+02	1,2E+04	2,1E+01	3,3E-06	6,4E-06	3,7E-08	1,1E-07
104	114-26-1	Propoxur	2,1E+02	9,2E+01	1,7E-05	1,8E+03	3,2E+01	4,5E-05	3,2E-06	2,2E-07	5,8E-07
105	10061-02-6	trans-1,3-dichloropropene	1,1E+02	-8,4E+01	3,1E+03	2,7E+03	1,0E+02	6,7E-06	9,5E-07	2,3E-07	1,0E-06
106	80844-07-1	Etofenprox	3,8E+02	3,7E+01	2,8E-05	1,0E-03	1,1E+07	3,1E-05	1,3E-07	4,3E-08	1,3E-07
107	107-18-6	ALLYL ALCOHOL	5,8E+01	-1,3E+02	3,5E+03	1,0E+06	1,5E+00	1,5E-05	3,0E-06	9,9E-07	3,0E-06
108	1582-09-8	Trifluralin	3,4E+02	4,9E+01	2,6E-02	5,0E-01	2,2E+05	4,2E-05	1,3E-07	2,7E-07	1,3E-07
109	126-99-8	2-CHLOR-1,3-BUTADIENE	8,9E+01	-1,3E+02	2,8E+04	4,8E+02	3,4E+02	1,2E-05	1,1E-07	3,7E-08	1,1E-07
110	75-65-0	TERT-BUTYL ALCOHOL	7,4E+01	2,5E+01	5,5E+03	1,0E+06	2,2E+00	5,4E-07	1,1E-07	4,4E-08	1,1E-07
111	13457-18-6	Pyrazophos	3,7E+02	5,2E+01	4,6E-05	4,2E+00	6,3E+03	5,6E-05	8,0E-07	6,7E-08	2,1E-07
112	66215-27-8	Cyromazine	1,7E+02	2,2E+02	4,5E-07	1,3E+04	8,7E-01	5,1E-05	5,2E-08	2,8E-08	8,6E-08
113	74-85-1	Ethylene	2,8E+01	-1,7E+02	1,0E+07	2,6E+02	1,3E+01	4,3E-06	1,5E-06	4,9E-07	1,5E-06
114	21087-64-9	Metribuzin	2,1E+02	1,3E+02	5,3E+05	1,2E+03	5,0E+01	9,8E-07	1,2E-07	4,0E-08	4,7E-08
115	002032-65-7	Methiocarb	2,3E+02	1,2E+02	1,6E-02	3,0E+01	8,3E+02	6,8E-06	3,4E-07	4,1E-08	1,3E-07
116	56-38-2	Parathion-ethyl	2,9E+02	6,0E+00	6,0E-04	1,2E+01	6,3E+03	4,5E-05	4,2E-07	1,7E-07	3,9E-07

	CAS	Name	g/mol MW	oC Tmelt	Pa VP 25o	mg/L S 25o	- K_{OW}	s-1 kdeg(air)25o	s-1 kwater	s-1 ksed	s-1ksoil
117	1024-57-3	Heptachlor epoxide	3,9E+02	1,6E+02	5,8E-04	2,8E-01	1,4E+05	5,8E-06	2,7E-08	3,0E-08	3,4E-08
118	24017-47-8	Triazophos	3,1E+02	3,2E+00	2,8E-04	3,7E+01	2,8E+03	5,6E-05	2,3E-07	4,0E-08	1,2E-07
119	100-42-5	Styrene	1,0E+02	-3,1E+01	8,0E+02	3,0E+02	1,1E+03	2,6E-05	4,1E-07	1,3E-07	4,1E-07
120	108-90-7	monochlorobenzene	1,1E+02	-4,6E+01	1,6E+03	4,8E+02	6,3E+02	4,4E-07	9,9E-08	2,6E-08	7,9E-08
121	126-98-7	METHYLACRYLONITRILE	6,7E+01	-3,6E+01	9,5E+03	2,5E+04	4,8E+00	2,9E-06	2,2E-07	7,9E-09	2,0E-08
122	75-05-8	ACETONITRILE	4,1E+01	-4,4E+01	1,2E+04	7,4E+04	4,6E-01	2,5E-08	5,7E-07	1,9E-07	5,7E-07
123	107-13-1	acrylonitrile	5,3E+01	-8,4E+01	1,1E+04	7,6E+04	1,8E+00	1,6E-06	1,5E-06	4,9E-07	1,5E-06
124	319-85-7	beta-HCH (beta-BHC)	2,9E+02	3,1E+02	6,5E-05	1,6E+00	6,9E+03	3,5E-06	1,3E-07	1,8E-07	1,3E-07
125	8018-01-7	Mancozeb	2,7E+02	2,0E+02	1,8E-08	6,2E+00	2,1E+01	1,1E-04	4,0E-06	5,2E-07	1,6E-06
126	91-59-8	2-AMINONAPHTHALENE	1,4E+02	1,1E+02	2,5E-01	4,5E+01	2,2E+02	1,1E-04	5,3E-07	3,6E-08	1,1E-07
127	1014-69-3	Desmetryn	2,1E+02	8,5E+01	1,9E-04	6,2E+02	2,4E+02	7,2E-05	2,5E-07	2,9E-07	8,9E-07
128	79-06-1	ACRYLAMIDE	7,1E+01	8,5E+01	9,3E-01	6,4E+05	2,1E-01	2,9E-05	6,1E-06	6,1E-07	6,1E-06
129	133-07-3	Folpet	3,0E+02	1,8E+02	1,3E-03	1,0E+00	4,3E+03	7,2E-06	2,0E-08	6,4E-09	2,0E-08
130	71751-41-2	Abamectine	8,7E+02	1,5E+02	2,0E-07	5,0E+00	2,8E+04	1,0E-04	2,9E-07	9,3E-08	2,9E-07
131	75-01-4	vinylchloride = chloroethene	6,3E+01	-1,5E+02	3,5E+05	2,8E+03	2,4E+01	3,3E-06	1,1E-07	3,7E-08	1,1E-07
132	60-29-7	Ethyl ether (diethyl ether)	7,4E+01	-1,2E+02	7,2E+04	6,1E+03	7,8E+00	1,1E-05	3,5E-07	1,4E-07	3,5E-07
133	95-63-6	1,2,4-TRIMETHYLBENZENE	1,2E+02	-4,4E+01	2,7E+02	5,7E+01	6,0E+03	2,0E-05	6,0E-07	1,9E-07	5,7E-07
134	98-07-7	BENZOIC TRICHLORIDE (BENZOTRICHLORIDE)	2,0E+02	-4,9E+00	3,1E+01	5,3E+01	7,9E+03	1,8E-07	6,3E-02	6,3E-02	6,3E-02
135	137-26-8	Thiram	2,4E+02	1,5E+02	1,3E-03	3,0E+01	5,4E+01	3,0E-07	4,6E-07	4,5E-07	2,6E-07
136	99-65-0	M-DINITROBENZENE	1,7E+02	9,0E+01	1,2E-01	5,3E+02	3,1E+01	1,5E-08	4,2E-07	1,5E-06	1,1E-07
137	298-00-0	Parathion-methyl	2,6E+02	3,8E+01	2,0E-03	2,5E+01	1,0E+03	3,1E-05	8,6E-07	2,9E-06	2,8E-07

	CAS	Name	g/mol MW	oC Tmelt	Pa VP 25o	mg/L S 25o	- K_{OW}	s-1 kdeg(air)25o	s-1 kwater	s-1 ksed	s-1ksoil
138	80-62-6	METHYL METHACRYLATE	1,0E+02	-4,8E+01	5,1E+03	1,5E+04	2,4E+01	3,3E-05	5,7E-07	1,9E-07	5,7E-07
139	129-00-0	Pyrene	2,0E+02	1,6E+02	6,1E-04	1,4E-01	1,0E+05	4,0E-05	1,6E-04	4,1E-09	1,3E-08
140	75-29-6	2-Chloropropane	7,9E+01	1,2E+02	6,9E+04	2,9E+03	4,9E+01	3,2E-07	2,0E-08	7,9E-09	2,0E-08
141	52315-07-8	Cypermethrin	4,2E+02	8,1E+01	1,9E-07	4,0E-03	4,0E+06	1,9E-05	1,6E-06	5,0E-08	1,5E-07
142	100-41-4	Ethylbenzene	1,1E+02	-9,5E+01	1,3E+03	1,5E+02	1,3E+03	3,7E-06	1,5E-06	1,8E-07	1,5E-06
143	115-32-2	Dicofol	3,7E+02	7,8E+01	5,3E-05	1,3E+00	1,0E+05	2,7E-06	2,1E-07	1,6E-07	1,3E-07
144	109-86-4	2-METHOXYETHANOL	7,6E+01	-8,5E+01	6,3E+02	1,0E+06	1,7E-01	1,9E-05	7,2E-07	2,1E-07	4,6E-07
145	57-14-7	1,1-DIMETHYLHYDRAZINE	6,0E+01	-5,8E+01	1,4E+04	1,0E+06	6,5E-02	4,2E-05	6,1E-07	2,0E-07	6,1E-07
146	90-04-0	O-ANISIDINE	1,2E+02	5,8E+00	1,3E+01	6,5E+03	1,5E+01	6,1E-05	5,3E-07	3,7E-08	1,1E-07
147	106-89-8	1-CHLORO-2,3-EPOXYPROPANE	9,2E+01	-2,5E+01	2,2E+03	6,6E+04	2,8E+00	2,2E-07	1,6E-06	1,2E-06	1,6E-06
148	23103-98-2	Pirimicarb	2,4E+02	9,1E+01	9,7E-04	3,2E+03	5,0E+01	1,1E-04	6,6E-07	2,4E-08	7,4E-08
149	56-72-4	Coumaphos	3,6E+02	9,5E+01	1,8E-05	1,6E+00	1,1E+04	5,7E-05	2,0E-08	6,4E-10	2,0E-08
150	107-06-2	1,2-dichloroethane	9,9E+01	-3,5E+01	1,1E+04	8,5E+03	2,8E+01	1,1E-07	2,2E-08	2,3E-08	8,2E-08
151	118-74-1	Hexachlorobenzene	2,8E+02	2,3E+02	2,3E-03	5,0E-03	3,2E+05	8,6E-09	5,6E-09	1,8E-09	5,6E-09
152	53-70-3	Dibenz(a,h)anthracene	2,8E+02	8,7E+01	1,0E-08	8,1E-04	4,6E+06	7,5E-05	2,8E-06	4,5E-09	1,4E-08
153	26761-40-0	Diisodecylphtalate	4,5E+02	-4,6E+01	6,7E-05	1,0E-03	1,0E+08	4,9E-06	5,2E-07	4,5E-08	3,0E-07
154	107-21-1	ETHYLENE GLYCOL	6,2E+01	-1,3E+01	1,2E+01	1,0E+06	4,4E-02	3,9E-06	1,6E-06	5,3E-07	1,6E-06
155	27554-26-3	Diisooctylphtalate	3,9E+02	-4,6E+01	1,3E-04	1,0E-03	1,0E+08	4,9E-06	5,2E-07	4,5E-08	3,0E-07
156	2642-71-9	Azinphos-ethyl	3,5E+02	5,0E+01	4,5E-04	4,8E+00	1,5E+03	8,7E-05	6,9E-07	1,2E-07	9,6E-07
157	108-10-1	HEXONE	1,0E+02	-8,4E+01	2,6E+03	1,9E+04	2,0E+01	7,1E-06	3,0E-06	9,9E-07	3,0E-06
158	100-44-7	Benzylchloride = a-chlorotoluene	1,3E+02	-4,6E+01	1,6E+02	5,3E+02	2,0E+02	1,5E-06	3,5E-06	3,1E-06	3,5E-06
159	108-05-4	VINYL ACETATE	8,6E+01	-9,3E+01	1,2E+04	2,0E+04	5,4E+00	3,5E-06	1,1E-06	4,3E-07	1,1E-06
160	470-90-6	Chlorfenvinphos	3,6E+02	-1,9E+01	1,0E-04	1,2E+02	6,6E+03	2,7E-05	3,9E-07	7,2E-08	2,2E-07

	CAS	Name	g/mol MW	oC Tmelt	Pa VP 25o	mg/L S 25o	- K_{OW}	s-1 kdeg(air)25o	s-1 kwater	s-1 ksed	s-1ksoil
161	90-43-7	2-PHENYLPHENOL	1,7E+02	5,6E+01	3,0E+01	7,0E+02	1,2E+03	1,5E-05	3,4E-06	9,9E-07	3,0E-06
162	79-34-5	1,1,2,2-Tetrachloroethane	1,7E+02	-4,4E+01	7,0E+02	3,1E+03	2,5E+02	1,5E-07	2,9E-07	7,1E-07	1,3E-07
163	108-38-3	m-xylene	1,1E+02	-4,8E+01	1,1E+03	1,6E+02	1,6E+03	1,2E-05	5,7E-07	1,9E-07	5,7E-07
164	1563-66-2	Carbofuran	2,2E+02	1,5E+02	8,0E-05	3,5E+02	2,1E+02	4,2E-05	5,9E-07	4,5E-07	6,7E-07
165	56-55-3	Benzo[a]anthracene	2,3E+02	1,6E+02	2,8E-05	1,1E-02	8,1E+05	1,1E-04	1,1E-04	9,9E-09	3,0E-08
166	79-01-6	trichloroethylene	1,3E+02	-8,4E+01	9,7E+03	1,4E+03	3,1E+02	1,2E-06	1,6E-07	4,7E-08	4,8E-08
167	71-43-2	Benzene	7,8E+01	5,5E+00	1,3E+04	1,8E+03	1,5E+02	6,0E-07	9,0E-07	1,2E-07	7,6E-08
168	75-69-4	CFC-11	1,4E+02	-1,1E+02	1,1E+05	1,0E+03	3,4E+02	2,5E-10	3,3E-08	1,1E-08	3,3E-08
169	75-15-0	Carbon disulphide	7,6E+01	-1,1E+02	4,9E+04	2,4E+03	8,7E+01	8,9E-07	6,6E-07	6,4E-08	2,0E-07
170	319-84-6	alpha-HCH (alpha-BHC)	2,9E+02	1,6E+02	5,7E-03	3,4E+00	6,3E+03	3,5E-06	1,2E-07	4,8E-07	1,1E-07
171	97-63-2	ethyl methacrylate	1,1E+02	-7,5E+01	1,9E+03	2,6E+01	8,7E+01	6,9E-06	2,0E-08	7,9E-09	2,0E-08
172	1897-45-6	Chlorothalonil	2,7E+02	2,5E+02	1,3E-01	6,0E-01	4,4E+02	3,1E-09	6,6E-07	1,2E-07	3,8E-07
173	100-00-5	1-chloro-4-nitrobenzene	1,6E+02	8,3E+01	2,0E+00	3,4E+02	2,5E+02	3,0E-08	3,1E-08	1,0E-08	3,1E-08
174	72-54-8	DDD	3,2E+02	1,1E+02	1,3E-04	9,3E-02	1,3E+06	2,4E-06	4,8E-09	5,2E-08	4,7E-09
175	92-52-4	BIPHENYL	1,5E+02	6,9E+01	1,3E+00	7,1E+00	9,5E+03	2,9E-06	4,5E-03	8,0E-07	2,5E-06
176	74-87-3	Methyl chloride	5,0E+01	-9,7E+01	5,8E+05	6,4E+03	8,0E+00	2,2E-08	5,7E-07	1,9E-07	5,7E-07
177	96-33-3	METHYL ACRYLATE	8,6E+01	-7,5E+01	1,1E+04	4,9E+04	6,3E+00	1,2E-05	3,0E-06	9,9E-07	3,0E-06
178	330-55-2	Linuron	2,5E+02	9,4E+01	2,3E-02	7,5E+01	1,0E+03	6,5E-05	2,0E-07	3,7E-08	1,1E-07
179	143390-89-0	Kresoxim-metil	3,1E+02	9,9E+01	2,3E-06	2,0E+00	2,5E+03	1,9E-05	2,1E-07	7,0E-08	2,1E-07
180	205-99-2	Benzo(b)fluoranthene	2,5E+02	2,2E+02	4,6E-05	7,7E-03	1,9E+06	2,2E-05	2,4E-06	5,6E-09	1,7E-08
181	207-08-9	Benzo[k]fluoranthene	2,5E+02	2,2E+02	5,2E-08	8,0E-04	1,0E+06	2,9E-05	4,4E-06	1,9E-09	5,7E-09
182	106-49-0	p-toluidine	1,1E+02	4,4E+01	6,1E+01	1,0E+04	2,5E+01	4,6E-05	2,0E-08	7,9E-09	2,0E-08
183	106-50-3	P-PHENYLENEDIAMINE	1,1E+02	1,4E+02	1,3E+02	3,7E+04	5,0E-01	1,1E-04	1,4E-06	1,9E-07	5,7E-07
184	75-45-6	Chlorodifluoromethane (freon-22)	8,6E+01	-1,6E+02	1,0E+05	2,9E+03	1,2E+01	1,5E-09	7,1E-05	7,1E-05	2,0E-08

	CAS	Name	g/mol MW	oC Tmelt	Pa VP 25o	mg/L S 25o	- K_{OW}	s-1 kdeg(air)25o	s-1 kwater	s-1 ksed	s-1ksoil
185	127-18-4	tetrachloroethylene (PER)	1,7E+02	-1,9E+01	2,6E+03	2,6E+02	3,8E+02	8,4E-08	1,1E-07	2,0E-08	3,2E-08
186	67-64-1	Acetone	5,8E+01	-9,5E+01	3,0E+04	6,0E+05	6,0E-01	1,2E-07	3,0E-06	9,9E-07	3,0E-06
187	67-66-3	Trichloromethane =chloroform	1,2E+02	-6,4E+01	2,6E+04	8,2E+03	9,3E+01	5,2E-08	1,1E-07	5,3E-07	1,1E-07
188	66230-04-4	Esfenvalerete	4,2E+02	6,0E+01	2,0E-07	2,0E-03	1,7E+06	1,1E-05	1,3E-07	4,3E-08	1,3E-07
189	218-01-9	Chrysene	2,3E+02	2,6E+02	5,7E-07	2,0E-03	3,2E+05	4,0E-05	2,6E-05	4,3E-09	1,3E-08
190	82-68-8	pentachloronitrobenzene = quintozene	3,0E+02	1,5E+02	6,6E-03	4,4E-01	4,4E+04	3,7E-09	2,1E-08	4,1E-07	2,1E-08
191	106325-08-0	epoxiconazole	3,3E+02	1,4E+02	1,4E-05	7,3E-02	2,8E+03	9,7E-06	2,0E-08	6,4E-09	2,0E-08
192	52-68-6	Trichlorfon	2,6E+02	8,4E+01	1,0E-03	1,5E+05	3,2E+00	3,2E-06	4,4E-06	3,6E-06	2,9E-06
193	18181-80-1	Bromopropylate	4,3E+02	7,7E+01	1,1E-05	1,0E-01	2,5E+05	3,3E-06	3,0E-06	4,4E-08	1,4E-07
194	86-30-6	N-NITROSODIPHENYLAMINE	1,9E+02	6,7E+01	8,9E-02	3,5E+01	1,3E+03	4,6E-05	4,4E-07	1,4E-07	4,4E-07
195	67-63-0	ISOPROPYL ALCOHOL	6,0E+01	-8,8E+01	5,7E+03	1,0E+06	1,1E+00	4,5E-06	3,0E-06	9,9E-07	3,0E-06
196	106-42-3	p-xylene	1,1E+02	1,3E+01	1,2E+03	2,2E+02	1,5E+03	7,6E-06	5,7E-07	1,9E-07	5,7E-07
197	540-59-0	1,2-DICHLOROETHYLENE	9,7E+01	2,7E+02	4,5E+04	3,5E+03	1,2E+02	1,1E-06	1,1E-07	3,7E-08	1,1E-07
198	60168-88-9	Fenarimol	3,3E+02	1,2E+02	2,9E-05	1,4E+01	4,9E+03	2,0E-06	1,3E-07	4,3E-08	1,3E-07
199	75-25-2	Bromoform	2,5E+02	8,6E+00	7,9E+02	3,2E+03	2,3E+02	2,5E-08	1,1E-07	3,7E-08	1,1E-07
200	124-48-1	Chlorodibromomethane	2,1E+02	-2,2E+01	4,2E+03	3,6E+03	1,6E+02	3,1E-08	1,1E-07	1,1E-07	1,1E-07

Appendix E1: Physical-chemical input data for the 200 compounds used in this study.

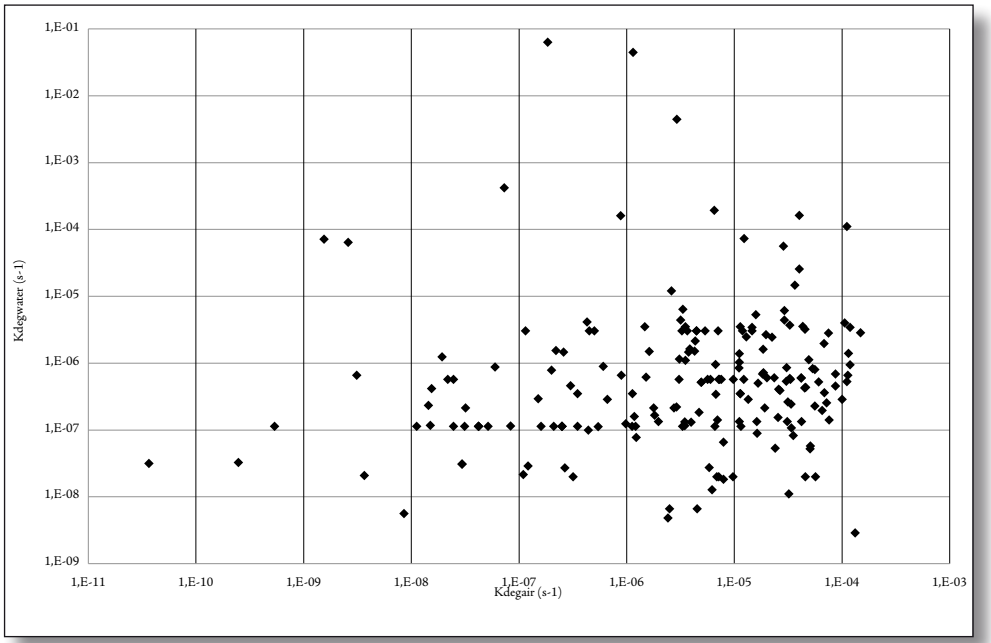


Figure E1-1: Air-water (K_h) and soil-water (K_p) partitioning properties of the 200 organic compounds used for the model calculations.

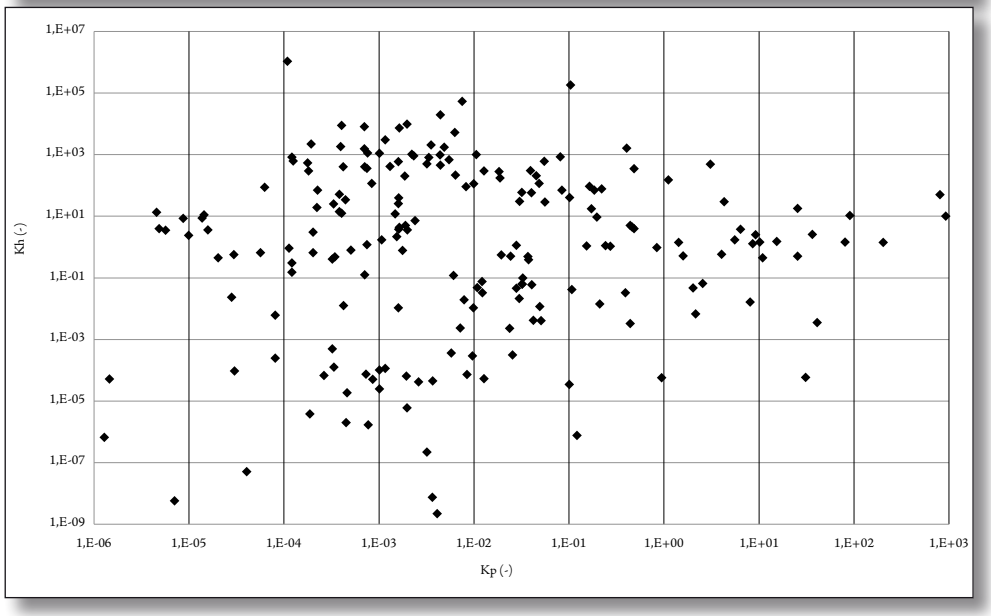
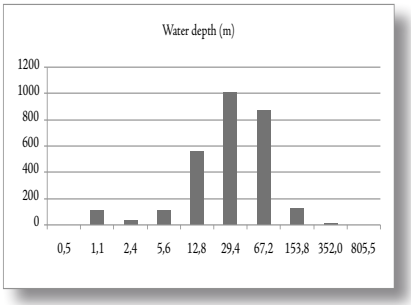
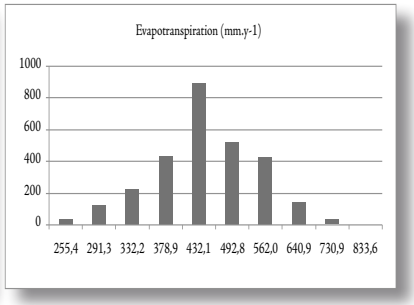
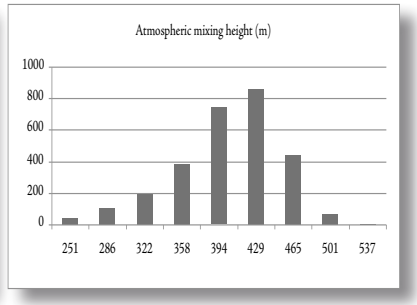
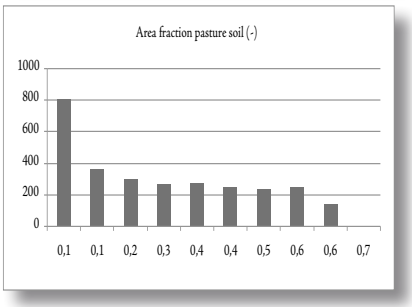


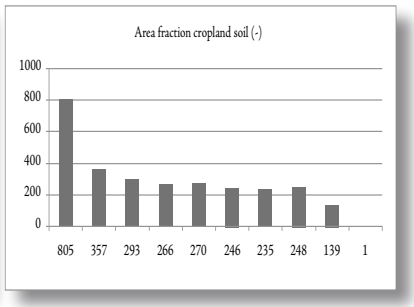
Figure E1-2: Degradation rate constants in air (K_{degair}) and water ($K_{degwater}$) of the 200 organic compounds used for the model calculations.

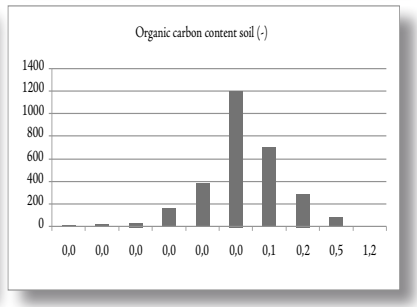

Water depth (m)
1200
1000
800
600
400
200
0
0,5 1,1 2,4 5,6 12,8 29,4 67,2 153,8 352,0 805,5

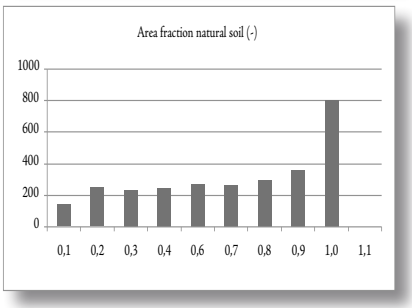

Evapotranspiration (mm.y-1)
1000
800
600
400
200
0
255,4 291,3 332,2 378,9 432,1 492,8 562,0 640,9 730,9 833,6

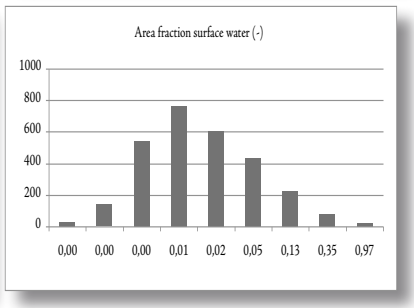

Atmospheric mixing height (m)
1000
800
600
400
200
0
251 286 322 358 394 429 465 501 537

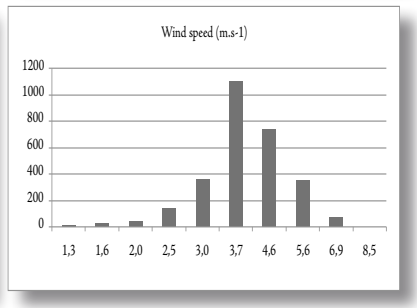

Area fraction pasture soil (-)
1000
800
600
400
200
0
0,1 0,1 0,2 0,3 0,4 0,4 0,5 0,6 0,6 0,7

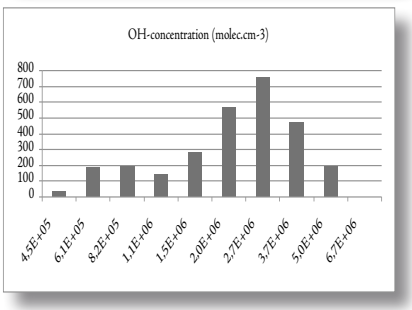

Area fraction cropland soil (-)
1000
800
600
400
200
0
805 357 293 266 270 246 235 248 139 1

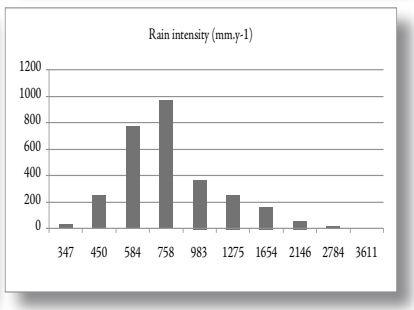

Organic carbon content soil (-)
1400
1200
1000
800
600
400
200
0
0,0 0,0 0,0 0,0 0,0 0,0 0,1 0,2 0,5 1,2

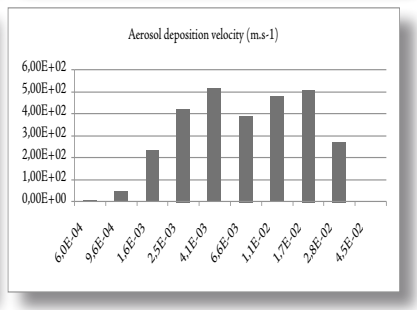

Area fraction natural soil (-)
1000
800
600
400
200
0
0,1 0,2 0,3 0,4 0,6 0,7 0,8 0,9 1,0 1,1

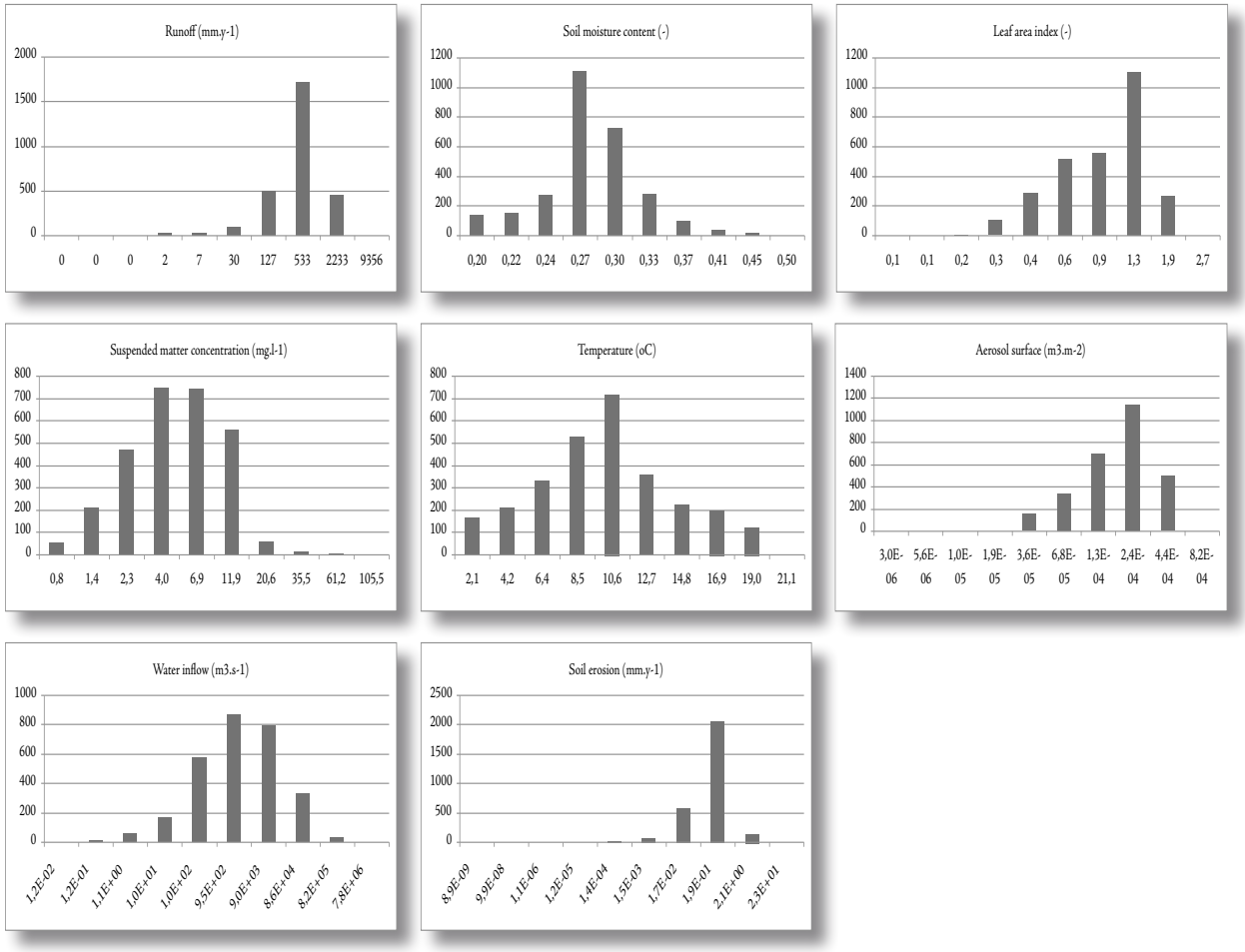

Area fraction surface water (-)
1000
800
600
400
200
0
0,00 0,00 0,00 0,01 0,02 0,05 0,13 0,35 0,97


Wind speed (m.s-1)
1200
1000
800
600
400
200
0
1,3 1,6 2,0 2,5 3,0 3,7 4,6 5,6 6,9 8,5


OH-concentration (molec.cm-3)
800
700
600
500
400
300
200
100
0
4,5E+05 6,1E+05 8,2E+05 1,1E+06 1,5E+06 2,0E+06 2,7E+06 3,7E+06 5,0E+06 6,7E+06


Rain intensity (mm.y-1)
1200
1000
800
600
400
200
0
347 450 584 758 983 1275 1654 2146 2784 3611


Aerosol deposition velocity (m.s-1)
6,00E+02
5,00E+02
4,00E+02
3,00E+02
2,00E+02
1,00E+02
0,00E+00
6,0E-04 9,6E-04 1,6E-03 2,5E-03 4,1E-03 6,6E-03 1,1E-02 1,7E-02 2,8E-02 4,5E-02



Appendix E2: Frequency distributions of the environmental input data.

Cell #	D	EROS	ET	FRP	FRC	FRN	FRW	H	OCTOP
	m	$mm.y^{-1}$	$mm.y^{-1}$	-	-	-	-	m	-
1	2.62E+01	5.06E-01	5.94E+02	2.94E-01	1.68E-01	5.38E-01	1.15E-03	3.95E+02	3.78E-03
2	1.38E+01	6.91E-02	4.90E+02	2.29E-01	1.31E-01	6.39E-01	1.15E-03	4.35E+02	1.84E-03
3	2.47E+01	3.98E-01	5.65E+02	2.76E-01	1.57E-01	5.67E-01	1.39E-03	4.17E+02	5.28E-03
4	2.85E+01	8.98E-02	5.11E+02	2.53E-01	1.45E-01	6.02E-01	1.58E-03	3.63E+02	1.07E-02
5	1.60E+01	1.22E-02	4.51E+02	2.75E-01	1.57E-01	5.69E-01	1.61E-03	4.43E+02	3.60E-03
6	5.24E+01	1.61E-02	4.28E+02	5.13E-01	2.93E-01	1.93E-01	1.69E-03	3.34E+02	3.84E-02
7	4.01E+01	2.17E-02	5.01E+02	1.98E-01	1.13E-01	6.89E-01	1.71E-03	3.85E+02	2.33E-02
8	2.71E+01	6.38E-03	6.78E+02	5.72E-02	3.27E-02	9.10E-01	2.24E-03	3.02E+02	3.86E-02
9	3.46E+01	6.91E-02	3.98E+02	4.10E-01	2.34E-01	3.56E-01	2.46E-03	3.93E+02	2.00E-02
10	3.38E+01	6.91E-02	4.00E+02	2.05E-01	1.17E-01	6.78E-01	2.48E-03	4.22E+02	2.00E-02
11	2.80E+01	3.05E-02	3.68E+02	2.11E-01	1.21E-01	6.68E-01	3.01E-03	4.17E+02	4.00E-02
12	5.20E+01	4.92E-02	5.15E+02	5.16E-01	2.95E-01	1.89E-01	3.02E-03	4.03E+02	5.91E-03
13	4.64E+01	3.11E-01	5.41E+02	2.43E-01	1.39E-01	6.18E-01	3.02E-03	4.35E+02	7.40E-03
14	2.89E+01	4.42E-02	4.82E+02	4.48E-01	2.56E-01	2.96E-01	3.04E-03	4.18E+02	2.31E-02
15	2.16E+01	6.74E-02	4.46E+02	2.23E-01	1.27E-01	6.50E-01	3.05E-03	4.09E+02	1.29E-02
16	3.29E+01	9.58E-02	4.80E+02	2.00E-01	1.14E-01	6.86E-01	3.16E-03	3.45E+02	1.47E-02
17	2.66E+01	3.61E-02	4.87E+02	3.87E-01	2.21E-01	3.92E-01	3.19E-03	4.46E+02	1.94E-02
18	2.57E+01	5.09E-02	4.15E+02	2.14E-01	1.22E-01	6.64E-01	3.61E-03	4.26E+02	3.66E-02
19	3.62E+01	8.39E-02	4.29E+02	5.61E-01	3.21E-01	1.18E-01	3.63E-03	3.68E+02	4.75E-03
20	2.36E+01	1.38E-01	5.75E+02	4.84E-01	2.76E-01	2.40E-01	3.70E-03	4.02E+02	1.99E-02
21	4.53E+01	1.61E-01	5.11E+02	1.20E-01	6.84E-02	8.12E-01	3.88E-03	3.72E+02	1.98E-02
22	3.29E+01	1.10E-01	5.69E+02	1.77E-01	1.01E-01	7.23E-01	4.07E-03	3.86E+02	2.54E-02
23	1.01E+01	6.91E-02	4.28E+02	5.34E-01	3.05E-01	1.60E-01	4.17E-03	4.26E+02	1.99E-02
24	2.49E+01	3.88E-02	4.96E+02	2.76E-01	1.58E-01	5.66E-01	4.20E-03	3.95E+02	3.67E-02
25	2.63E+01	3.76E-02	3.90E+02	3.28E-01	1.88E-01	4.84E-01	4.24E-03	4.35E+02	4.87E-02
26	2.15E+01	3.66E-02	5.08E+02	4.39E-01	2.51E-01	3.09E-01	4.27E-03	4.30E+02	1.81E-02
27	3.03E+01	1.38E-02	4.72E+02	2.87E-01	1.64E-01	5.50E-01	4.29E-03	3.20E+02	4.74E-02
28	3.91E+01	2.59E-01	4.64E+02	1.90E-01	1.08E-01	7.02E-01	4.30E-03	3.23E+02	8.56E-03
29	2.47E+01	1.70E-02	4.20E+02	3.71E-01	2.12E-01	4.17E-01	4.38E-03	4.64E+02	3.19E-02
30	4.16E+01	5.94E-02	3.46E+02	3.25E-01	1.86E-01	4.89E-01	4.58E-03	3.87E+02	9.08E-03
31	6.52E+00	6.91E-02	3.81E+02	3.64E-01	2.08E-01	4.28E-01	4.60E-03	3.90E+02	1.99E-02

OH	Q	R	SM	SPM	T	U10	AER	LAI	Aer.surf.	Inflow
cm^{-3}	$mm.y^{-1}$	$mm.y^{-1}$	-	$mg.l^{-1}$	°C	m/s	$m.s^{-1}$	$m^2.m^{-2}$	$m^2.m^{-3}$	$m^3.s^{-1}$
3.14E+06	4.01E+02	9.89E+02	2.66E-01	8.92E+00	9.65E+00	2.24E+00	1.47E-03	5.67E-01	1.74E-04	1.99E+02
2.90E+06	5.92E+02	1.15E+03	2.71E-01	1.06E+01	1.88E+01	3.11E+00	2.25E-03	7.78E-01	1.39E-04	2.31E+02
3.57E+06	4.00E+02	9.60E+02	2.79E-01	9.91E+00	1.71E+01	2.75E+00	2.05E-03	5.65E-01	1.69E-04	1.93E+02
3.82E+06	4.41E+02	9.24E+02	2.52E-01	8.27E+00	1.77E+01	4.13E+00	1.37E-03	1.00E+00	1.76E-04	1.86E+02
3.46E+06	6.71E+02	1.12E+03	2.69E-01	1.24E+01	1.82E+01	4.19E+00	1.94E-03	3.99E-01	1.60E-04	2.25E+02
7.65E+05	1.63E+02	5.90E+02	2.75E-01	1.61E+00	9.34E+00	5.51E+00	2.71E-03	1.22E+00	1.67E-04	1.19E+02
2.38E+06	2.72E+02	7.81E+02	2.74E-01	2.92E+00	1.11E+01	4.54E+00	2.11E-03	1.26E+00	1.72E-04	1.57E+02
2.64E+06	6.99E+02	1.39E+03	2.65E-01	6.42E+00	1.50E+01	4.38E+00	1.24E-03	7.78E-01	8.42E-05	2.79E+02
1.74E+06	1.17E+02	5.14E+02	2.75E-01	3.86E+00	6.08E+00	3.53E+00	5.78E-03	7.78E-01	1.74E-04	1.03E+02
1.80E+06	1.05E+02	5.06E+02	2.60E-01	3.37E+00	6.25E+00	3.42E+00	8.36E-03	1.07E+00	1.81E-04	1.02E+02
1.46E+06	2.13E+02	5.80E+02	2.79E-01	6.11E+00	7.44E+00	2.81E+00	1.25E-02	1.14E+00	2.21E-04	1.17E+02
4.25E+06	3.05E+02	8.34E+02	3.18E-01	7.71E+00	1.69E+01	4.04E+00	1.55E-03	3.84E-01	1.59E-04	1.68E+02
4.01E+06	2.06E+02	7.54E+02	2.86E-01	7.01E+00	1.55E+01	1.83E+00	3.22E-03	6.04E-01	1.61E-04	1.51E+02
2.19E+06	1.79E+02	6.59E+02	2.70E-01	3.23E+00	1.05E+01	4.31E+00	3.35E-03	1.09E+00	2.47E-04	1.32E+02
2.78E+06	2.17E+02	6.52E+02	3.05E-01	6.42E+00	1.47E+01	3.15E+00	3.46E-03	7.46E-01	1.91E-04	1.31E+02
3.36E+06	4.13E+02	8.80E+02	2.41E-01	6.54E+00	1.55E+01	3.87E+00	2.17E-03	6.79E-01	1.52E-04	1.77E+02
2.44E+06	1.29E+02	6.15E+02	2.67E-01	4.28E+00	1.13E+01	4.03E+00	9.16E-03	1.14E+00	2.16E-04	1.24E+02
2.02E+06	2.84E+02	6.91E+02	2.58E-01	4.92E+00	7.78E+00	3.37E+00	1.28E-02	1.12E+00	3.10E-04	1.39E+02
4.54E+06	2.72E+02	6.97E+02	2.59E-01	9.06E+00	1.74E+01	4.32E+00	1.40E-03	6.82E-01	1.86E-04	1.40E+02
2.82E+06	2.36E+02	8.01E+02	2.41E-01	3.47E+00	1.20E+01	4.63E+00	2.34E-03	9.50E-01	1.33E-04	1.61E+02
3.24E+06	1.28E+02	6.35E+02	2.78E-01	5.48E+00	1.54E+01	3.69E+00	3.12E-03	6.56E-01	1.74E-04	1.28E+02
3.17E+06	5.85E+02	1.16E+03	2.56E-01	6.20E+00	1.35E+01	2.85E+00	5.04E-03	1.05E+00	1.96E-04	2.32E+02
2.07E+06	4.40E+01	4.73E+02	2.74E-01	3.24E+00	8.01E+00	3.29E+00	5.61E-03	9.46E-01	2.20E-04	9.50E+01
1.83E+06	2.73E+02	7.70E+02	2.65E-01	3.93E+00	1.00E+01	3.85E+00	6.77E-03	1.06E+00	3.20E-04	1.55E+02
2.16E+06	2.74E+02	6.68E+02	2.52E-01	4.77E+00	7.95E+00	3.52E+00	1.21E-02	1.03E+00	3.76E-04	1.34E+02
2.98E+06	1.61E+02	6.64E+02	2.67E-01	3.95E+00	1.20E+01	4.32E+00	3.22E-03	1.05E+00	1.87E-04	1.33E+02
1.50E+06	3.29E+02	7.97E+02	2.90E-01	2.58E+00	9.89E+00	4.43E+00	1.84E-03	1.27E+00	1.71E-04	1.60E+02
3.86E+06	1.53E+02	6.04E+02	2.99E-01	8.50E+00	1.76E+01	4.59E+00	1.28E-03	4.78E-01	5.01E-05	1.21E+02
2.44E+06	1.46E+02	5.69E+02	3.02E-01	6.11E+00	1.00E+01	2.58E+00	7.34E-03	1.13E+00	3.02E-04	1.14E+02
3.55E+06	3.06E+01	3.75E+02	2.90E-01	7.57E+00	1.50E+01	3.53E+00	3.13E-03	3.15E-01	9.70E-05	7.53E+01
1.54E+06	1.92E+02	5.71E+02	2.65E-01	4.73E+00	4.99E+00	3.25E+00	7.23E-03	7.78E-01	1.61E-04	1.15E+02

Cell #	D	EROS	ET	FRP	FRC	FRN	FRW	H	OCTOP
	m	$mm.y^{-1}$	$mm.y^{-1}$	-	-	-	-	m	-
32	1.58E+01	1.34E-02	3.60E+02	3.48E-01	1.99E-01	4.53E-01	4.63E-03	4.26E+02	2.86E-02
33	3.14E+01	8.55E-02	4.99E+02	5.92E-01	3.38E-01	7.03E-02	4.74E-03	3.62E+02	4.06E-03
34	2.17E+01	6.91E-02	4.22E+02	4.29E-02	2.45E-02	9.33E-01	4.75E-03	4.22E+02	1.99E-02
35	2.17E+01	4.85E-02	3.94E+02	4.48E-01	2.56E-01	2.95E-01	4.85E-03	4.37E+02	4.32E-02
36	3.14E+01	4.61E-02	4.67E+02	3.84E-01	2.19E-01	3.97E-01	4.87E-03	3.71E+02	5.68E-02
37	2.01E+01	3.24E-02	4.51E+02	3.00E-01	1.71E-01	5.29E-01	4.94E-03	3.95E+02	5.23E-02
38	5.07E+01	1.41E-01	5.20E+02	3.26E-01	1.86E-01	4.88E-01	5.05E-03	3.96E+02	1.48E-02
39	2.19E+01	1.74E-02	4.42E+02	5.46E-01	3.12E-01	1.41E-01	5.07E-03	3.45E+02	2.70E-02
40	2.05E+01	4.80E-03	5.26E+02	2.61E-02	1.49E-02	9.59E-01	5.12E-03	2.77E+02	5.49E-02
41	1.91E+01	2.25E-02	4.00E+02	2.65E-01	1.51E-01	5.84E-01	5.30E-03	4.31E+02	4.88E-02
42	7.91E+01	5.15E-03	3.93E+02	1.77E-01	1.01E-01	7.23E-01	5.36E-03	3.82E+02	3.26E-02
43	2.30E+01	3.44E-02	4.10E+02	3.74E-01	2.14E-01	4.12E-01	5.39E-03	3.94E+02	4.89E-02
44	2.39E+01	2.30E-02	5.11E+02	1.16E-01	6.61E-02	8.18E-01	5.47E-03	4.32E+02	4.63E-02
45	9.99E+00	1.08E-02	4.26E+02	4.05E-01	2.31E-01	3.63E-01	5.48E-03	4.26E+02	2.00E-02
46	2.77E+01	5.18E-02	5.05E+02	2.32E-01	1.33E-01	6.35E-01	5.65E-03	3.77E+02	3.58E-02
47	1.52E+00	6.91E-02	2.55E+02	5.35E-02	3.06E-02	9.16E-01	5.88E-03	3.86E+02	1.97E-02
48	4.19E+01	1.18E-01	5.90E+02	3.29E-01	1.88E-01	4.84E-01	5.91E-03	3.36E+02	1.04E-02
49	4.69E+01	1.38E-01	5.08E+02	2.83E-01	1.62E-01	5.56E-01	6.12E-03	3.71E+02	2.46E-02
50	2.13E+01	3.36E-02	4.23E+02	3.18E-01	1.82E-01	5.00E-01	6.30E-03	4.35E+02	2.24E-02
51	3.14E+01	5.11E-02	5.09E+02	2.50E-01	1.43E-01	6.08E-01	6.33E-03	4.09E+02	3.30E-02
52	3.41E+01	9.49E-03	4.71E+02	1.30E-01	7.44E-02	7.96E-01	6.33E-03	3.11E+02	1.17E-01
53	1.63E+01	7.64E-02	5.67E+02	2.61E-01	1.49E-01	5.90E-01	6.42E-03	3.60E+02	4.20E-02
54	4.26E+01	5.49E-02	4.89E+02	2.89E-01	1.65E-01	5.45E-01	6.47E-03	3.89E+02	2.22E-02
55	3.55E+01	6.11E-02	3.94E+02	3.58E-01	2.05E-01	4.37E-01	6.55E-03	4.02E+02	1.27E-02
56	3.07E+01	1.74E-02	4.80E+02	3.97E-01	2.27E-01	3.76E-01	6.57E-03	3.54E+02	6.96E-03
57	1.48E+01	6.91E-02	3.84E+02	5.85E-02	3.34E-02	9.08E-01	6.59E-03	3.98E+02	1.99E-02
58	1.70E+01	2.72E-02	3.67E+02	4.66E-01	2.66E-01	2.67E-01	6.59E-03	4.41E+02	5.49E-02
59	3.27E+01	4.88E-02	3.89E+02	3.30E-01	1.89E-01	4.81E-01	6.61E-03	4.12E+02	1.72E-02
60	1.44E+01	7.11E-02	5.62E+02	3.72E-01	2.13E-01	4.15E-01	7.16E-03	3.92E+02	1.60E-02
61	3.61E+01	2.53E-01	5.08E+02	2.32E-01	1.32E-01	6.36E-01	7.27E-03	3.54E+02	2.09E-02
62	3.35E+01	1.36E-02	6.33E+02	6.71E-02	3.84E-02	8.95E-01	7.31E-03	3.32E+02	4.82E-02

OH	*Q*	*R*	*SM*	*SPM*	*T*	*U10*	*AER*	*LAI*	*Aer.surf.*	*Inflow*
cm^{-3}	*mm.y^{-1}*	*mm.y^{-1}*	*-*	*mg.l^{-1}*	*°C*	*m/s*	*m.s^{-1}*	*m^2.m^{-2}*	*m^2.m^{-3}*	*m^3.s^{-1}*
2.56E+06	1.45E+02	4.91E+02	3.00E-01	7.79E+00	1.02E+01	2.58E+00	1.08E-02	1.22E+00	2.57E-04	9.87E+01
3.56E+06	2.89E+02	7.89E+02	2.82E-01	8.73E+00	1.85E+01	4.11E+00	1.36E-03	4.45E-01	1.36E-04	1.59E+02
1.47E+06	9.26E+01	5.14E+02	2.73E-01	3.86E+00	7.36E+00	3.32E+00	9.39E-03	9.15E-01	2.16E-04	1.03E+02
2.21E+06	1.92E+02	5.91E+02	2.55E-01	4.25E+00	8.23E+00	4.34E+00	7.09E-03	9.80E-01	3.75E-04	1.19E+02
1.92E+06	3.63E+02	8.28E+02	2.55E-01	3.05E+00	9.41E+00	3.91E+00	3.63E-03	1.19E+00	3.49E-04	1.66E+02
1.82E+06	3.06E+02	7.57E+02	2.73E-01	4.29E+00	9.58E+00	3.02E+00	9.46E-03	1.16E+00	3.49E-04	1.52E+02
3.90E+06	3.74E+02	9.09E+02	2.60E-01	6.77E+00	1.46E+01	3.40E+00	4.33E-03	1.01E+00	1.89E-04	1.83E+02
1.34E+06	1.22E+02	5.66E+02	2.95E-01	1.97E+00	1.00E+01	4.74E+00	3.22E-03	1.15E+00	2.26E-04	1.14E+02
1.96E+06	7.05E+02	1.23E+03	2.60E-01	2.87E+00	1.05E+01	5.28E+00	1.11E-03	1.37E+00	1.05E-04	2.48E+02
2.20E+06	1.19E+02	5.20E+02	2.72E-01	3.36E+00	7.62E+00	3.42E+00	8.93E-03	9.13E-01	2.89E-04	1.05E+02
1.89E+06	3.30E+02	7.32E+02	2.44E-01	8.07E+00	1.03E+01	2.94E+00	7.31E-03	1.25E+00	1.73E-04	1.47E+02
2.12E+06	2.04E+02	6.15E+02	2.63E-01	4.14E+00	8.51E+00	3.98E+00	9.75E-03	1.14E+00	3.52E-04	1.24E+02
2.13E+06	4.27E+02	9.39E+02	2.56E-01	6.81E+00	1.14E+01	3.69E+00	6.80E-03	1.28E+00	1.57E-04	1.89E+02
1.80E+06	1.41E+02	5.62E+02	2.67E-01	4.40E+00	7.34E+00	3.53E+00	1.09E-02	1.01E+00	2.40E-04	1.13E+02
2.45E+06	6.58E+02	1.14E+03	2.64E-01	9.09E+00	1.05E+01	2.28E+00	7.76E-03	1.15E+00	2.50E-04	2.29E+02
4.81E+05	3.27E+02	3.65E+02	2.43E-01	1.18E+00	9.65E+00	3.52E+00	1.57E-02	7.78E-01	5.50E-05	7.34E+01
3.52E+06	8.15E+02	1.40E+03	2.41E-01	9.08E+00	1.69E+01	3.82E+00	1.86E-03	7.79E-01	1.81E-04	2.81E+02
2.54E+06	5.01E+02	9.99E+02	2.78E-01	7.51E+00	1.27E+01	3.73E+00	6.68E-03	1.05E+00	1.31E-04	2.01E+02
2.50E+06	9.30E+01	5.18E+02	3.14E-01	5.54E+00	1.23E+01	2.69E+00	7.97E-03	1.00E+00	2.39E-04	1.04E+02
2.24E+06	4.00E+02	9.04E+02	2.80E-01	5.68E+00	1.05E+01	3.09E+00	8.92E-03	1.27E+00	2.33E-04	1.82E+02
1.48E+06	5.05E+02	9.72E+02	2.92E-01	2.25E+00	9.45E+00	4.75E+00	1.51E-03	1.23E+00	1.32E-04	1.95E+02
2.30E+06	5.08E+02	1.04E+03	2.56E-01	3.07E+00	1.16E+01	5.11E+00	2.05E-03	1.15E+00	1.24E-04	2.09E+02
2.87E+06	3.73E+02	8.70E+02	2.89E-01	7.29E+00	1.19E+01	3.57E+00	4.40E-03	9.05E-01	1.20E-04	1.75E+02
3.26E+06	3.79E+00	3.99E+02	2.91E-01	1.04E+01	1.33E+01	3.52E+00	6.40E-03	3.87E-01	1.31E-04	8.01E+01
3.95E+06	2.29E+02	6.75E+02	2.65E-01	5.71E+00	1.58E+01	3.38E+00	3.05E-03	7.02E-01	1.95E-04	1.36E+02
1.30E+06	1.64E+02	5.47E+02	2.68E-01	3.27E+00	5.15E+00	3.49E+00	1.26E-02	1.12E+00	1.49E-04	1.10E+02
2.45E+06	1.23E+02	4.88E+02	2.33E-01	3.08E+00	8.18E+00	3.49E+00	5.15E-03	9.76E-01	3.32E-04	9.81E+01
3.19E+06	4.67E+01	4.34E+02	2.83E-01	6.20E+00	1.33E+01	3.37E+00	4.22E-03	5.14E-01	1.13E-04	8.73E+01
2.69E+06	1.92E+02	7.53E+02	2.65E-01	5.01E+00	1.32E+01	3.59E+00	2.63E-03	9.12E-01	1.50E-04	1.51E+02
2.59E+06	7.56E+02	1.28E+03	2.63E-01	7.03E+00	1.28E+01	2.51E+00	4.42E-03	1.14E+00	2.07E-04	2.56E+02
3.15E+06	8.86E+02	1.52E+03	2.70E-01	6.88E+00	1.40E+01	3.97E+00	2.24E-03	7.78E-01	1.16E-04	3.05E+02

Cell #	D	EROS	ET	FRP	FRC	FRN	FRW	H	OCTOP
	m	$mm.y^{-1}$	$mm.y^{-1}$	-	-	-	-	m	-
63	1.20E+01	2.82E-03	3.94E+02	2.47E-01	1.41E-01	6.12E-01	7.34E-03	3.70E+02	9.07E-02
64	3.56E+01	2.98E-01	4.45E+02	3.77E-01	2.15E-01	4.08E-01	7.39E-03	3.48E+02	5.33E-03
65	2.10E+01	1.39E-02	3.77E+02	3.38E-01	1.93E-01	4.69E-01	7.68E-03	4.39E+02	2.59E-02
66	2.67E+01	1.91E-02	3.96E+02	2.95E-01	1.69E-01	5.36E-01	7.75E-03	4.35E+02	3.61E-02
67	3.12E+01	4.88E-02	4.05E+02	2.65E-01	1.52E-01	5.83E-01	7.89E-03	3.56E+02	1.24E-02
68	1.87E+01	5.24E-02	5.15E+02	2.99E-01	1.71E-01	5.30E-01	7.98E-03	3.97E+02	2.34E-02
69	1.49E+01	6.91E-02	4.07E+02	1.58E-01	9.02E-02	7.52E-01	8.89E-03	4.10E+02	1.98E-02
70	3.96E+01	1.09E-02	5.70E+02	2.55E-02	1.46E-02	9.60E-01	8.93E-03	2.63E+02	1.05E-01
71	1.65E+01	2.06E-02	3.99E+02	3.10E-01	1.77E-01	5.12E-01	9.10E-03	3.73E+02	4.68E-02
72	3.21E+01	1.06E-01	6.69E+02	7.41E-02	4.24E-02	8.84E-01	9.23E-03	3.13E+02	3.09E-02
73	2.89E+01	1.43E-02	3.37E+02	2.35E-01	1.35E-01	6.30E-01	9.54E-03	4.08E+02	6.79E-03
74	3.75E+01	2.84E-01	5.85E+02	3.52E-01	2.01E-01	4.47E-01	9.58E-03	3.71E+02	1.73E-02
75	2.95E+01	2.36E-01	5.37E+02	3.36E-01	1.92E-01	4.72E-01	9.61E-03	3.92E+02	1.68E-02
76	3.32E+01	9.34E-02	5.05E+02	2.27E-01	1.30E-01	6.43E-01	9.77E-03	3.63E+02	3.65E-02
77	2.31E+01	1.29E-01	5.82E+02	2.52E-01	1.44E-01	6.03E-01	1.02E-02	3.36E+02	1.05E-02
78	1.26E+01	6.52E-02	4.63E+02	3.71E-01	2.12E-01	4.17E-01	1.04E-02	3.82E+02	4.29E-02
79	4.27E+00	6.91E-02	3.24E+02	9.18E-02	5.25E-02	8.56E-01	1.05E-02	3.96E+02	1.95E-02
80	1.64E+01	2.67E-02	4.32E+02	4.44E-01	2.54E-01	3.02E-01	1.06E-02	4.32E+02	2.55E-02
81	4.64E+01	6.19E-02	4.11E+02	3.02E-01	1.72E-01	5.26E-01	1.08E-02	4.31E+02	1.53E-02
82	2.95E+01	4.91E-02	5.12E+02	2.36E-01	1.35E-01	6.30E-01	1.09E-02	4.48E+02	2.83E-02
83	1.29E+01	1.36E-02	4.04E+02	3.45E-01	1.97E-01	4.58E-01	1.14E-02	4.19E+02	4.68E-02
84	5.78E+00	6.91E-02	4.06E+02	3.82E-01	2.18E-01	4.00E-01	1.14E-02	4.33E+02	1.94E-02
85	1.16E+01	1.47E-02	4.17E+02	4.21E-01	2.41E-01	3.38E-01	1.14E-02	3.25E+02	6.56E-02
86	3.72E+01	2.89E-02	4.45E+02	2.25E-01	1.29E-01	6.46E-01	1.18E-02	3.62E+02	4.93E-02
87	2.49E+01	2.61E-02	4.11E+02	4.13E-01	2.36E-01	3.51E-01	1.31E-02	4.56E+02	3.42E-02
88	3.57E+00	6.91E-02	2.58E+02	4.47E-02	2.55E-02	9.30E-01	1.34E-02	3.60E+02	1.92E-02
89	1.61E+01	1.81E-01	5.00E+02	3.70E-01	2.12E-01	4.18E-01	1.37E-02	3.43E+02	5.27E-03
90	1.04E+01	2.14E-02	4.01E+02	4.97E-01	2.84E-01	2.19E-01	1.38E-02	4.41E+02	1.46E-02
91	9.79E+00	2.83E-02	4.01E+02	4.45E-01	2.55E-01	3.00E-01	1.39E-02	4.17E+02	4.52E-02
92	7.90E+01	6.05E-02	4.92E+02	2.50E-01	1.43E-01	6.07E-01	1.40E-02	4.03E+02	2.89E-02
93	3.18E+01	1.02E-01	4.43E+02	2.62E-01	1.50E-01	5.89E-01	1.45E-02	3.93E+02	1.15E-02

OH	*Q*	*R*	*SM*	*SPM*	*T*	*U10*	*AER*	*LAI*	*Aer.surf.*	*Inflow*
cm⁻³	*mm.y⁻¹*	*mm.y⁻¹*	*-*	*mg.l⁻¹*	*°C*	*m/s*	*m.s⁻¹*	*m².m⁻²*	*m².m⁻³*	*m³.s⁻¹*
1.14E+06	5.45E+02	9.51E+02	2.39E-01	1.40E+00	6.08E+00	4.65E+00	3.31E-03	4.69E-01	1.12E-04	1.91E+02
4.14E+06	1.47E+02	5.88E+02	2.81E-01	9.84E+00	1.69E+01	3.89E+00	1.76E-03	4.96E-01	9.49E-05	1.18E+02
2.51E+06	8.65E+01	4.50E+02	2.76E-01	6.90E+00	1.10E+01	2.81E+00	6.16E-03	9.37E-01	2.65E-04	9.05E+01
2.14E+06	2.70E+02	6.77E+02	2.88E-01	7.82E+00	1.05E+01	2.60E+00	1.06E-02	9.89E-01	2.15E-04	1.36E+02
4.28E+06	1.90E+02	6.03E+02	2.64E-01	6.26E+00	1.66E+01	3.67E+00	1.69E-03	7.14E-01	1.39E-04	1.21E+02
2.37E+06	3.30E+02	8.53E+02	2.65E-01	6.32E+00	1.23E+01	3.80E+00	6.16E-03	1.06E+00	1.43E-04	1.71E+02
1.69E+06	1.93E+02	5.99E+02	2.72E-01	3.48E+00	6.44E+00	3.23E+00	6.94E-03	9.47E-01	1.92E-04	1.20E+02
1.77E+06	8.55E+02	1.39E+03	2.62E-01	2.92E+00	1.05E+01	5.45E+00	1.31E-03	1.23E+00	6.78E-05	2.80E+02
2.22E+06	3.07E+02	7.02E+02	2.66E-01	7.12E+00	7.76E+00	3.45E+00	1.04E-02	1.01E+00	2.72E-04	1.41E+02
3.01E+06	9.16E+02	1.55E+03	2.66E-01	8.70E+00	1.46E+01	4.35E+00	1.80E-03	8.28E-01	1.11E-04	3.12E+02
3.57E+06	1.24E+02	4.53E+02	2.83E-01	6.16E+00	1.67E+01	3.19E+00	2.00E-03	2.78E-01	1.31E-04	9.09E+01
4.16E+06	4.94E+02	1.07E+03	2.46E-01	7.10E+00	1.57E+01	3.03E+00	1.81E-03	9.33E-01	1.82E-04	2.15E+02
3.59E+06	3.40E+02	8.69E+02	2.51E-01	5.95E+00	1.34E+01	2.75E+00	5.73E-03	1.08E+00	2.24E-04	1.75E+02
2.98E+06	4.25E+02	9.22E+02	2.72E-01	8.04E+00	1.27E+01	3.65E+00	4.15E-03	8.95E-01	1.17E-04	1.85E+02
3.74E+06	3.90E+02	9.70E+02	2.29E-01	8.73E+00	1.65E+01	3.73E+00	2.27E-03	5.95E-01	1.12E-04	1.95E+02
2.25E+06	4.25E+02	8.82E+02	2.29E-01	2.10E+00	8.65E+00	5.33E+00	2.27E-03	1.18E+00	2.31E-04	1.77E+02
5.19E+05	2.99E+02	6.94E+02	2.33E-01	1.48E+00	1.86E+00	3.62E+00	1.46E-02	7.78E-01	6.74E-05	1.39E+02
2.21E+06	1.23E+02	5.49E+02	2.59E-01	7.04E+00	1.06E+01	2.43E+00	6.58E-03	1.06E+00	2.65E-04	1.10E+02
2.97E+06	1.00E+02	5.11E+02	2.78E-01	5.84E+00	1.37E+01	2.02E+00	5.28E-03	8.77E-01	1.80E-04	1.03E+02
3.16E+06	4.04E+02	9.19E+02	2.60E-01	6.17E+00	1.36E+01	4.33E+00	6.60E-03	7.76E-01	1.74E-04	1.85E+02
1.96E+06	1.95E+02	6.01E+02	2.53E-01	2.85E+00	6.93E+00	3.56E+00	8.97E-03	1.08E+00	2.18E-04	1.21E+02
2.29E+06	6.46E+01	4.71E+02	3.00E-01	4.74E+00	8.60E+00	3.64E+00	3.49E-03	7.78E-01	2.41E-04	9.46E+01
1.49E+06	3.66E+02	7.83E+02	2.51E-01	2.07E+00	7.03E+00	4.15E+00	2.91E-03	8.45E-01	1.50E-04	1.57E+02
2.07E+06	5.89E+02	1.02E+03	2.59E-01	8.84E+00	7.50E+00	2.90E+00	6.43E-03	1.05E+00	2.76E-04	2.05E+02
2.75E+06	9.98E+01	5.06E+02	2.89E-01	5.76E+00	1.00E+01	2.94E+00	5.48E-03	1.08E+00	3.37E-04	1.02E+02
6.01E+05	1.91E+02	4.44E+02	2.68E-01	9.42E-01	9.65E+00	3.91E+00	7.25E-03	3.30E-01	6.35E-05	8.93E+01
4.33E+06	1.17E+02	6.18E+02	2.57E-01	8.35E+00	1.70E+01	3.96E+00	1.70E-03	5.19E-01	6.31E-05	1.24E+02
2.24E+06	4.29E+01	4.43E+02	3.21E-01	3.76E+00	9.45E+00	3.78E+00	6.84E-03	7.54E-01	2.32E-04	8.89E+01
2.26E+06	1.57E+02	5.57E+02	2.65E-01	1.70E+00	8.46E+00	5.24E+00	4.38E-03	1.15E+00	2.44E-04	1.12E+02
2.70E+06	6.31E+02	1.15E+03	2.43E-01	6.14E+00	9.64E+00	2.19E+00	7.57E-03	8.38E-01	2.55E-04	2.31E+02
3.33E+06	1.72E+02	6.03E+02	2.29E-01	8.38E+00	1.53E+01	3.42E+00	2.59E-03	5.37E-01	9.52E-05	1.21E+02

Cell #	D	EROS	ET	FRP	FRC	FRN	FRW	H	OCTOP
	m	mm.y^{-1}	mm.y^{-1}	-	-	-	-	m	-
94	6.64E+01	6.91E-02	4.52E+02	1.02E-01	5.82E-02	8.40E-01	1.54E-02	3.52E+02	3.46E-02
95	1.03E+01	2.80E-02	3.73E+02	3.74E-01	2.14E-01	4.13E-01	1.60E-02	4.21E+02	5.73E-02
96	6.89E+00	6.91E-02	3.34E+02	1.09E-01	6.25E-02	8.28E-01	1.63E-02	3.89E+02	1.96E-02
97	6.40E+01	4.17E-01	5.88E+02	1.76E-01	1.01E-01	7.23E-01	1.66E-02	3.83E+02	7.63E-03
98	4.99E+01	1.89E-02	4.66E+02	6.81E-02	3.89E-02	8.93E-01	1.66E-02	2.72E+02	1.92E-01
99	1.30E+01	4.72E-03	4.89E+02	2.66E-01	1.52E-01	5.81E-01	1.67E-02	3.29E+02	6.22E-02
100	1.26E+01	6.91E-02	4.18E+02	2.54E-01	1.45E-01	6.01E-01	1.71E-02	4.11E+02	1.96E-02
101	4.87E+01	3.85E-02	4.68E+02	2.11E-01	1.20E-01	6.69E-01	1.75E-02	3.60E+02	4.35E-02
102	1.11E+02	1.02E-01	4.96E+02	2.54E-01	1.45E-01	6.01E-01	1.81E-02	3.68E+02	3.80E-02
103	9.50E+00	5.94E-03	4.05E+02	4.24E-01	2.42E-01	3.34E-01	1.83E-02	4.05E+02	7.42E-02
104	9.01E+01	7.17E-02	4.92E+02	1.92E-01	1.10E-01	6.98E-01	1.84E-02	4.10E+02	3.81E-02
105	9.52E+01	1.27E-01	4.97E+02	2.24E-01	1.28E-01	6.47E-01	1.85E-02	3.59E+02	2.17E-02
106	7.89E+00	6.91E-02	3.11E+02	1.06E-01	6.08E-02	8.33E-01	1.87E-02	3.74E+02	1.95E-02
107	5.30E+00	6.91E-02	3.57E+02	1.12E-01	6.42E-02	8.23E-01	1.87E-02	3.84E+02	1.96E-02
108	9.01E+00	2.23E-02	4.03E+02	3.90E-01	2.23E-01	3.88E-01	1.96E-02	4.08E+02	5.36E-02
109	5.95E+00	6.91E-02	3.67E+02	1.38E-01	7.86E-02	7.84E-01	2.05E-02	3.88E+02	1.95E-02
110	8.24E+00	2.02E-02	3.80E+02	3.22E-01	1.84E-01	4.94E-01	2.18E-02	3.64E+02	5.61E-02
111	3.65E+01	6.91E-02	3.70E+02	3.15E-02	1.80E-02	9.51E-01	2.52E-02	3.06E+02	9.32E-02
112	1.19E+01	6.91E-02	2.70E+02	1.82E-02	1.04E-02	9.71E-01	2.55E-02	3.66E+02	3.27E-01
113	8.40E+00	2.26E-02	4.12E+02	4.02E-01	2.30E-01	3.68E-01	2.59E-02	3.79E+02	6.31E-02
114	9.00E+00	1.09E-01	4.34E+02	4.55E-01	2.60E-01	2.85E-01	2.74E-02	3.95E+02	4.77E-02
115	3.96E+00	6.91E-02	3.76E+02	2.77E-01	1.58E-01	5.65E-01	2.86E-02	3.66E+02	1.92E-02
116	7.66E+00	3.31E-03	3.93E+02	1.88E-01	1.07E-01	7.05E-01	2.90E-02	3.87E+02	2.57E-02
117	2.76E+01	3.48E-03	5.43E+02	1.96E-02	1.12E-02	9.69E-01	2.92E-02	2.49E+02	1.30E-01
118	7.70E+00	1.67E-03	3.86E+02	4.39E-02	2.51E-02	9.31E-01	3.00E-02	3.86E+02	2.00E-02
119	1.83E+01	5.94E-03	5.00E+02	1.98E-02	1.13E-02	9.69E-01	3.02E-02	2.51E+02	8.46E-02
120	1.07E+01	1.73E-02	3.49E+02	4.72E-01	2.70E-01	2.58E-01	3.58E-02	4.24E+02	1.47E-02
121	4.48E+01	6.91E-02	3.34E+02	2.00E-02	1.14E-02	9.69E-01	4.71E-02	3.27E+02	5.40E-02
122	9.33E+00	6.91E-02	3.02E+02	5.97E-02	3.41E-02	9.06E-01	4.78E-02	3.86E+02	2.15E-01
123	9.25E+00	6.91E-02	3.48E+02	1.27E-01	7.28E-02	8.00E-01	4.83E-02	4.16E+02	8.56E-02
124	9.77E+00	6.91E-02	3.97E+02	4.64E-01	2.65E-01	2.70E-01	4.98E-02	3.74E+02	1.10E-02

OH	*Q*	*R*	*SM*	*SPM*	*T*	*U10*	*AER*	*LAI*	*Aer.surf.*	*Inflow*
cm^{-3}	*mm.y^{-1}*	*mm.y^{-1}*	*-*	*mg.l^{-1}*	*°C*	*m/s*	*m.s^{-1}*	*m^2.m^{-2}*	*m^2.m^{-3}*	*m^3.s^{-1}*
1.81E+06	1.02E+03	1.47E+03	2.41E-01	9.86E+00	1.20E+01	2.99E+00	4.69E-03	1.30E+00	1.74E-04	2.96E+02
2.24E+06	1.30E+02	4.98E+02	2.29E-01	2.85E+00	8.91E+00	3.71E+00	1.17E-02	9.60E-01	2.98E-04	1.00E+02
5.22E+05	3.36E+02	6.87E+02	2.54E-01	1.90E+00	2.39E+00	3.59E+00	1.90E-02	7.78E-01	8.66E-05	1.38E+02
3.33E+06	5.45E+02	1.11E+03	2.76E-01	9.27E+00	1.63E+01	1.55E+00	1.28E-03	7.20E-01	1.74E-04	2.24E+02
1.40E+06	8.57E+02	1.33E+03	3.45E-01	2.03E+00	8.40E+00	4.68E+00	2.91E-03	8.11E-01	7.85E-05	2.67E+02
1.72E+06	2.13E+02	7.05E+02	2.53E-01	2.82E+00	9.80E+00	4.46E+00	3.43E-03	9.98E-01	3.05E-04	1.42E+02
1.74E+06	5.33E+01	4.71E+02	2.66E-01	4.02E+00	7.29E+00	2.88E+00	8.79E-03	8.90E-01	2.06E-04	9.47E+01
2.31E+06	5.78E+02	1.05E+03	2.70E-01	7.27E+00	9.36E+00	2.53E+00	8.05E-03	1.14E+00	2.82E-04	2.10E+02
2.60E+06	7.53E+02	1.25E+03	2.54E-01	7.35E+00	8.54E+00	2.64E+00	7.49E-03	9.55E-01	2.13E-04	2.51E+02
1.45E+06	2.45E+02	6.46E+02	2.60E-01	2.37E+00	6.38E+00	3.53E+00	6.96E-03	1.03E+00	1.67E-04	1.30E+02
2.51E+06	5.87E+02	1.07E+03	2.64E-01	7.02E+00	1.03E+01	3.43E+00	9.04E-03	1.28E+00	1.84E-04	2.15E+02
2.74E+06	4.55E+02	9.36E+02	2.64E-01	8.18E+00	1.32E+01	2.02E+00	2.72E-03	9.36E-01	1.60E-04	1.88E+02
6.82E+05	2.70E+02	5.83E+02	2.71E-01	1.27E+00	1.16E+00	3.59E+00	6.57E-03	4.82E-01	7.36E-05	1.17E+02
7.50E+05	3.26E+02	6.83E+02	2.88E-01	3.23E+00	3.57E+00	3.11E+00	1.51E-02	7.30E-01	1.12E-04	1.37E+02
2.09E+06	1.01E+02	5.04E+02	2.33E-01	2.75E+00	9.07E+00	4.22E+00	8.47E-03	1.06E+00	2.98E-04	1.01E+02
8.67E+05	2.48E+02	6.14E+02	2.74E-01	3.21E+00	4.46E+00	3.09E+00	1.62E-02	9.20E-01	1.22E-04	1.23E+02
1.94E+06	2.63E+02	6.39E+02	2.37E-01	2.30E+00	8.13E+00	4.46E+00	4.38E-03	9.25E-01	2.26E-04	1.28E+02
7.37E+05	1.05E+03	1.39E+03	1.89E-01	1.24E+00	5.97E+00	4.91E+00	2.30E-03	3.82E-01	3.51E-05	2.79E+02
7.73E+05	2.72E+02	5.37E+02	3.17E-01	1.12E+00	8.27E-01	3.52E+00	9.94E-03	4.44E-01	5.26E-05	1.08E+02
2.03E+06	2.36E+02	6.46E+02	2.64E-01	2.83E+00	7.57E+00	3.84E+00	5.65E-03	1.17E+00	2.23E-04	1.30E+02
2.00E+06	4.16E+02	8.48E+02	1.95E-01	2.54E+00	8.12E+00	5.63E+00	2.67E-03	6.16E-01	1.46E-04	1.70E+02
1.58E+06	2.80E+02	6.56E+02	2.65E-01	4.42E+00	4.48E+00	3.03E+00	1.44E-02	7.78E-01	1.79E-04	1.32E+02
1.21E+06	2.02E+02	5.94E+02	2.72E-01	2.72E+00	5.58E+00	3.39E+00	8.50E-03	1.13E+00	1.57E-04	1.19E+02
1.66E+06	7.78E+02	1.31E+03	2.90E-01	2.64E+00	1.03E+01	5.11E+00	1.37E-03	7.76E-01	5.60E-05	2.63E+02
8.67E+05	2.24E+02	6.09E+02	2.84E-01	2.97E+00	5.05E+00	3.28E+00	1.13E-02	9.62E-01	1.29E-04	1.22E+02
1.75E+06	6.15E+02	1.12E+03	2.77E-01	2.62E+00	9.60E+00	4.99E+00	1.62E-03	1.29E+00	9.06E-05	2.24E+02
2.98E+06	1.21E+01	3.59E+02	3.07E-01	5.68E+00	1.12E+01	3.53E+00	4.27E-03	7.39E-01	2.71E-04	7.21E+01
1.14E+06	8.34E+02	1.16E+03	1.83E-01	1.97E+00	5.01E+00	5.18E+00	4.90E-03	4.12E-01	7.03E-05	2.33E+02
9.21E+05	2.56E+02	5.62E+02	2.48E-01	1.88E+00	2.81E+00	3.49E+00	7.30E-03	5.19E-01	7.00E-05	1.13E+02
1.26E+06	1.74E+02	5.25E+02	2.65E-01	1.92E+00	6.85E+00	5.51E+00	1.48E-02	6.96E-01	1.32E-04	1.05E+02
2.25E+06	3.77E+01	4.34E+02	3.43E-01	3.39E+00	1.04E+01	3.96E+00	2.55E-03	7.78E-01	2.21E-04	8.72E+01

Cell #	D	EROS	ET	FRP	FRC	FRN	FRW	H	OCTOP
	m	$mm.y^{-1}$	$mm.y^{-1}$	-	-	-	-	m	-
125	5.99E+00	6.91E-02	4.12E+02	4.46E-01	2.55E-01	2.99E-01	5.70E-02	3.86E+02	1.88E-02
126	1.61E+01	6.91E-02	3.04E+02	8.21E-02	4.69E-02	8.71E-01	6.17E-02	4.07E+02	1.14E-01
127	1.21E+01	6.19E-02	3.87E+02	1.44E-01	8.20E-02	7.74E-01	6.76E-02	4.21E+02	1.09E-01
128	7.99E+00	6.91E-02	3.47E+02	4.13E-02	2.36E-02	9.35E-01	6.78E-02	4.04E+02	1.01E-01
129	7.26E+00	4.01E-03	3.91E+02	3.19E-01	1.83E-01	4.98E-01	7.05E-02	3.89E+02	1.17E-01
130	8.14E+00	6.91E-02	3.05E+02	3.36E-02	1.92E-02	9.47E-01	8.68E-02	3.63E+02	1.77E-02
131	7.22E+00	6.91E-02	3.13E+02	2.67E-01	1.52E-01	5.81E-01	9.47E-02	4.33E+02	8.19E-02
132	8.18E+00	8.82E-03	3.62E+02	2.21E-02	1.26E-02	9.65E-01	1.31E-01	4.11E+02	8.02E-02
133	1.13E+01	6.91E-02	3.36E+02	1.08E-01	6.18E-02	8.30E-01	1.50E-01	4.01E+02	1.68E-02
134	1.68E+01	6.91E-02	3.42E+02	1.12E-01	6.40E-02	8.24E-01	1.73E-01	4.08E+02	9.30E-02
135	1.18E+01	6.91E-02	3.27E+02	3.33E-02	1.90E-02	9.48E-01	1.78E-01	3.60E+02	2.65E-02
136	1.04E+01	6.91E-02	3.45E+02	1.81E-01	1.03E-01	7.16E-01	1.82E-01	3.82E+02	1.61E-02
137	1.20E+01	6.91E-02	3.63E+02	5.13E-02	2.93E-02	9.19E-01	2.44E-01	3.75E+02	1.49E-02

Appendix E3: environmental input parameter values for each of the 137 regions on a 250x250 km scale.

OH	*Q*	*R*	*SM*	*SPM*	*T*	*U10*	*AER*	*LAI*	*Aer.surf.*	*Inflow*
cm^{-3}	$mm.y^{-1}$	$mm.y^{-1}$	-	$mg.l^{-1}$	°C	*m/s*	$m.s^{-1}$	$m^2.m^{-2}$	$m^2.m^{-3}$	$m^3.s^{-1}$
1.92E+06	6.01E+01	4.72E+02	2.75E-01	4.28E+00	7.49E+00	3.40E+00	3.94E-03	7.78E-01	2.13E-04	9.48E+01
8.31E+05	1.80E+02	4.82E+02	2.64E-01	1.87E+00	3.55E+00	3.67E+00	1.59E-02	4.80E-01	5.87E-05	9.68E+01
1.65E+06	3.09E+02	6.99E+02	2.67E-01	2.54E+00	7.58E+00	4.75E+00	6.27E-03	8.15E-01	1.53E-04	1.40E+02
1.54E+06	2.89E+02	6.37E+02	2.37E-01	2.89E+00	4.86E+00	3.54E+00	6.66E-03	5.29E-01	8.79E-05	1.28E+02
1.02E+06	3.85E+02	7.74E+02	2.91E-01	4.23E+00	5.69E+00	4.03E+00	6.40E-03	8.55E-01	1.26E-04	1.56E+02
6.14E+05	2.67E+02	5.76E+02	2.72E-01	3.27E+00	7.42E-01	3.74E+00	1.06E-02	3.89E-01	6.86E-05	1.16E+02
1.51E+06	1.56E+02	4.68E+02	2.67E-01	3.56E+00	5.81E+00	4.19E+00	1.29E-02	6.08E-01	9.27E-05	9.41E+01
1.38E+06	2.83E+02	6.41E+02	2.36E-01	5.16E+00	4.26E+00	3.31E+00	1.45E-02	5.34E-01	1.06E-04	1.29E+02
5.80E+05	3.03E+02	6.37E+02	3.01E-01	4.94E+00	2.30E+00	3.41E+00	1.18E-02	5.66E-01	8.54E-05	1.28E+02
1.42E+06	3.71E+02	7.08E+02	2.69E-01	5.96E+00	5.81E+00	4.21E+00	1.09E-02	5.45E-01	8.77E-05	1.42E+02
6.10E+05	3.02E+02	6.28E+02	2.62E-01	5.45E+00	2.14E+00	3.31E+00	1.39E-02	4.72E-01	8.40E-05	1.26E+02
1.27E+06	3.30E+02	6.74E+02	2.79E-01	5.88E+00	3.44E+00	3.42E+00	1.07E-02	7.78E-01	1.31E-04	1.36E+02
1.08E+06	2.43E+02	6.07E+02	2.96E-01	1.00E+01	4.16E+00	2.91E+00	1.27E-02	6.11E-01	1.47E-04	1.22E+02

	D	*EROS*	*ET*	*FRP*	*FRC*	*FRN*	*FRW*	*H*	*OC*	*OH*	*Q*
D	1.00										
EROS	0.18	1.00									
ET	0.59	0.13	1.00								
FRP	0.11	0.12	0.22	1.00							
FRC	0.12	0.13	0.22	1.00	1.00						
FRN	-0.10	-0.10	-0.20	-0.99	-0.98	1.00					
FRW	-0.40	-0.08	-0.49	-0.39	-0.40	0.38	1.00				
H	-0.19	0.13	-0.28	0.45	0.45	-0.41	-0.10	1.00			
OC	-0.13	-0.44	-0.24	-0.38	-0.38	0.37	0.40	-0.22	1.00		
OH	0.55	0.35	0.62	0.48	0.48	-0.46	-0.48	0.07	-0.59	1.00	
Q	0.25	0.01	0.37	-0.41	-0.40	0.42	0.00	-0.48	0.24	-0.08	1.00
R	0.49	0.05	0.69	-0.28	-0.27	0.29	-0.15	-0.54	0.10	0.18	0.86
SM	0.03	-0.10	-0.02	0.11	0.11	-0.12	-0.04	0.07	-0.16	0.06	-0.36
SPM	0.52	0.30	0.49	0.28	0.30	-0.25	-0.24	0.17	-0.57	0.71	0.01
T	0.55	0.24	0.66	0.37	0.37	-0.36	-0.58	-0.08	-0.58	0.89	0.03
U10	-0.14	-0.28	0.03	-0.12	-0.14	0.07	0.05	-0.43	0.34	-0.17	0.13
AER	-0.43	-0.08	-0.64	-0.13	-0.12	0.16	0.39	0.51	0.29	-0.59	-0.21
LAI	0.18	-0.32	0.34	0.19	0.20	-0.17	-0.28	0.01	0.28	-0.09	0.17
Aers	0.12	-0.13	0.14	0.58	0.59	-0.56	-0.29	0.46	0.01	0.17	-0.23
Inflow	0.49	0.05	0.69	-0.28	-0.27	0.29	-0.15	-0.54	0.10	0.18	0.86
K_p	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K_h	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
k_{degair}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$k_{degw/s}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Explanation of the parameter names: D = water depth, EROS = soil erosion, ET = evapotranspiration, FRP = fraction pasture soil, FRC = fraction cropland soil, / FRN = fraction natural soil, FRW = fraction surface water, H = atmospheric mixing height, OC = organic carbon content in soil, Q = runoff from soil, / R = rain intensity, SM = soil moisture content, SPM = suspended particulate matter concentration, T = atmospheric temperature, U10 = wind speed, / AER = aerosol deposition velocity, LAI = leaf area index, Inflow = water inflow in cell, K_p = soil-water partitioning coefficient, K_h = air-water partitioning coefficient, / k_{degair} = degradation rate constant in air, $k_{degw/s}$ = degradation rate constant in water.

Parameter units can be found in Table 12.

	R	*SM*	*SPM*	*T*	*U10*	*AER*	*LAI*	*Aers.*	*Inflow*	K_p	K_h	k_{degair}	$k_{degw/s}$
	1.00												
	-0.27	*1.00*											
	0.23	*0.17*	*1.00*										
	0.29	*0.08*	*0.63*	*1.00*									
	0.13	*-0.19*	*-0.50*	*-0.05*	*1.00*								
	-0.45	*-0.01*	*-0.21*	*-0.70*	*-0.35*	*1.00*							
	0.20	*-0.02*	*-0.03*	*-0.04*	*0.00*	*0.10*	*1.00*						
	-0.17	*0.02*	*0.18*	*0.05*	*-0.27*	*0.20*	*0.54*	*1.00*					
	1.00	*-0.27*	*0.23*	*0.29*	*0.13*	*-0.45*	*0.20*	*-0.17*	*1.00*				
	0.00	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*1.00*			
	0.00	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.07*	*1.00*		
	0.00	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*-0.14*	*-0.11*	*1.00*	
	0.00	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*-0.10*	*-0.12*	*0.06*	*1.00*

Appendix E4a: Correlation matrix of the environmental and chemical input parameters.

Appendix E4b: Data transformation for stepwise multiple regression analysis

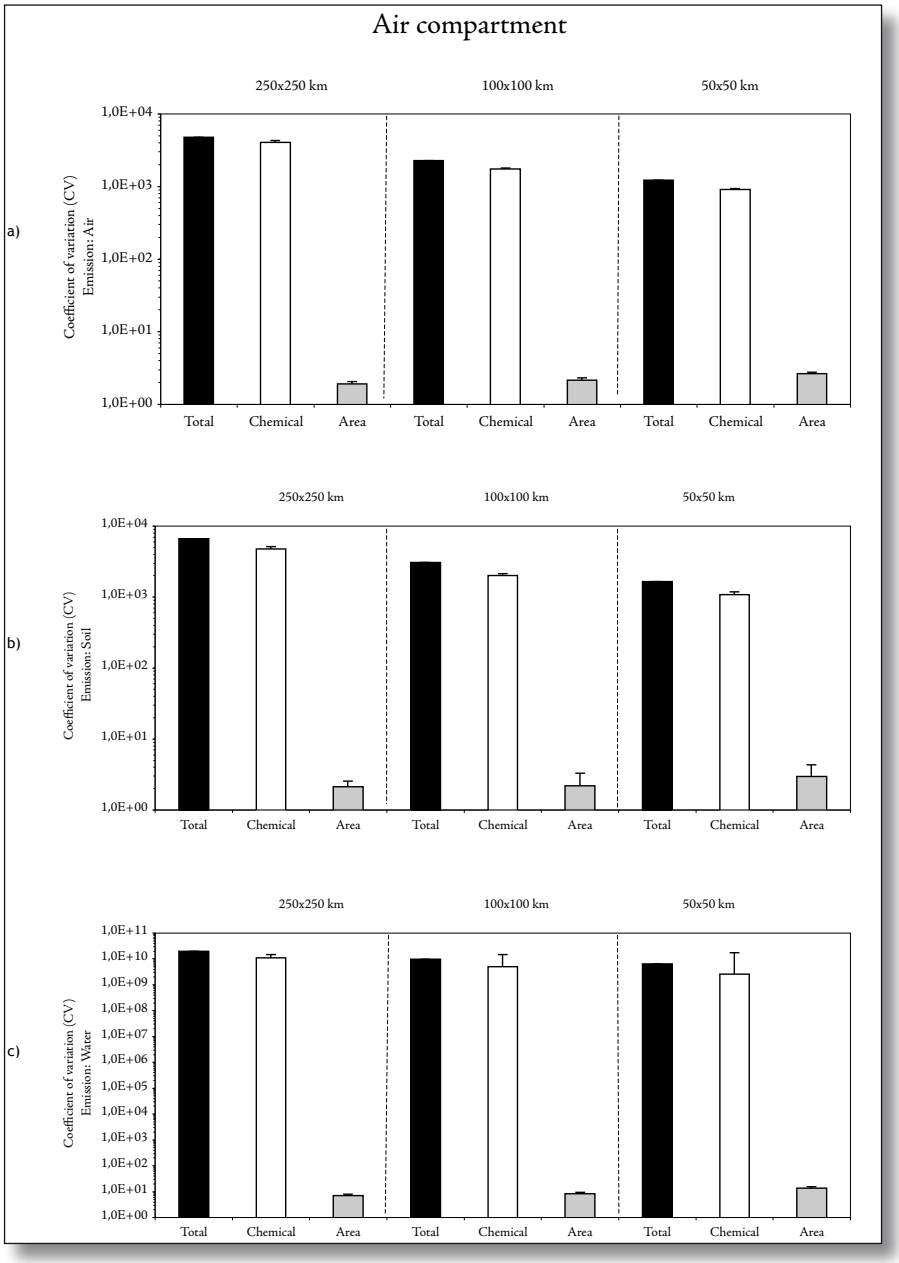
Correlations
Parameters that were not taken into account in the stepwise multiple regression analysis due to mutual correlation:
ET, FRP, FRN, OH, Q, SPM, AER, Inflow

Data transformation stepwise multiple regression analysis
Parameters that were log-transformed before performing stepwise multiple regression analysis:
D, EROS, R, U10, LAI, Aersurf, Concentration

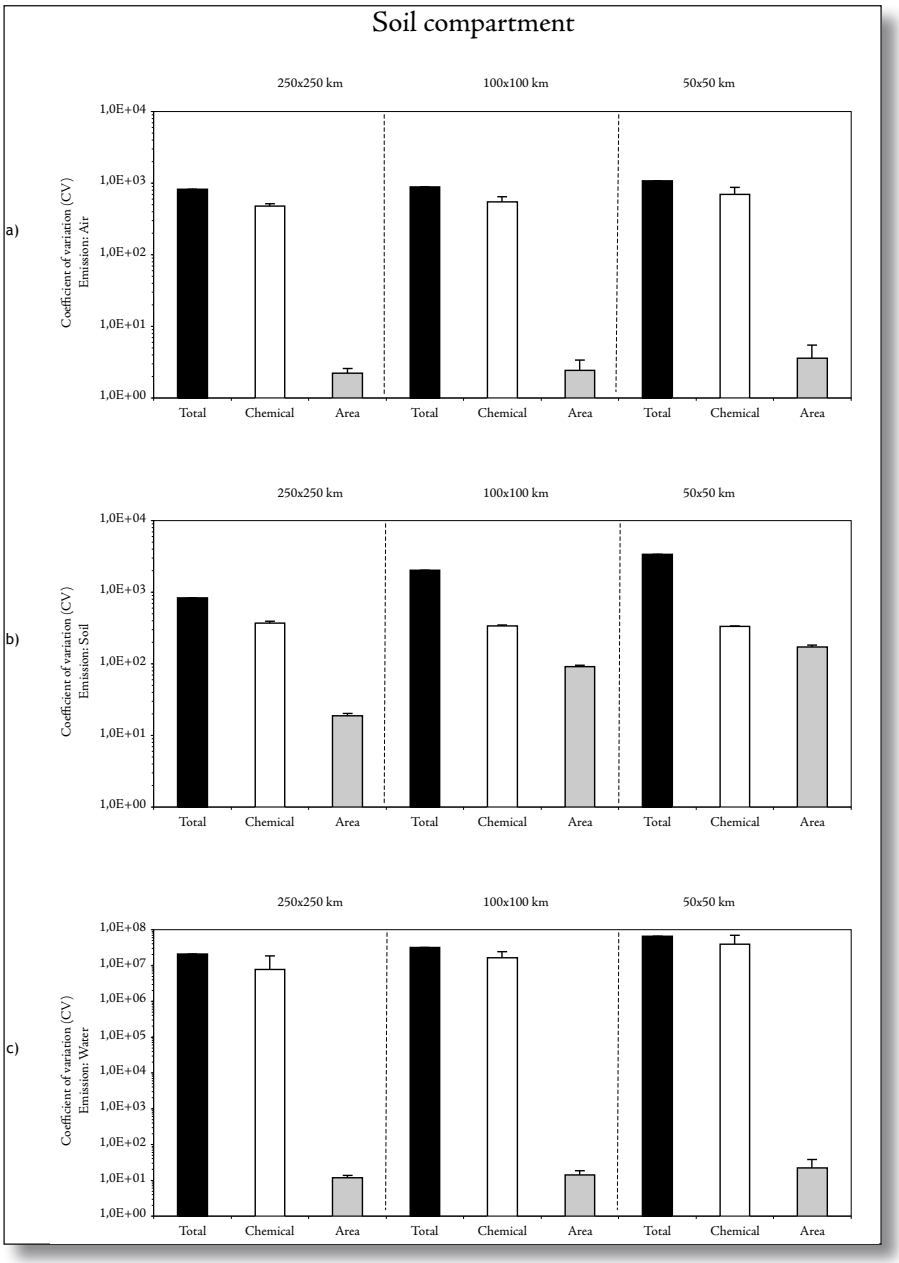
Parameters of which the values were transformed from 0 to 1 to -∞ to +∞ before performing stepwise multiple regression analysis: log(x/1-x):
FRC, FRW, OCTOP, SM, Aersurf, K_p, K_h, K_{degair}, $K_{degw/s}$

Appendix E5: Average concentration ranges on the 250x250, 100x100 and 50x50 km scales

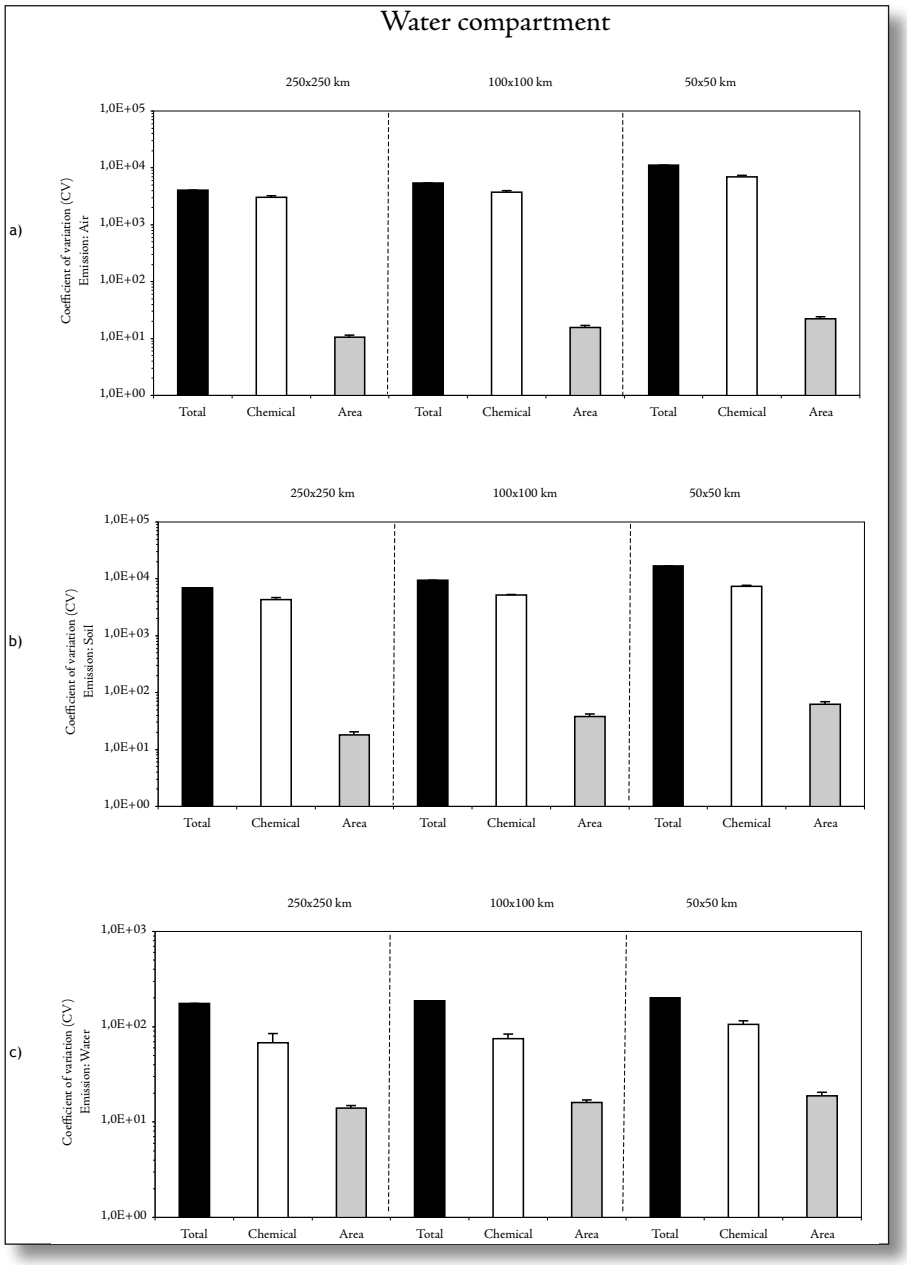
The graphs show the average concentration ranges (CR) for the environmental concentrations in Europe, for three emission scenarios. Concentration ranges are given for the total concentration variation (CRtotal, black bars), the concentration variation caused by the variation in substance properties (CRchemical; white bars), and the concentration variation caused by differences in environmental characteristics (CRarea; grey bars). The error bars indicate the 95% CR-levels.
Appendix E5-1: Air compartment,
Appendix E5-2: Soil compartment,
Appendix E5-3: Water compartment.



Appendix E5-1: Air compartment



Appendix E5-2: Soil compartment



Appendix E5-3: Water compartment

10 Summary

Chemical substances can be harmful for the human health or for the functioning of ecosystems. Numerous chemical substances are on the market, with different emission patterns and different physical-chemical properties. Due to these differences, the substances do not behave similarly in the environment after being emitted. To be able to estimate or predict their environmental fate, multimedia mass balance models are often used. Principally, in these models, the environment is represented as a set of homogeneous boxes, each representing a specific part or compartment of the environment (i.e. air, water, soil, biota). The concentration of a chemical in a certain compartment can be calculated by solving a set of mass balance equations that describe the processes of emissions, degradation and inter-compartment transfer. Due to the rapid development of geographical information systems (GIS), spatially resolved multimedia fate models were developed since the 1990s. Nowadays, many of the models do take into account spatial environmental variation, but at the same time, their complexity increases as well as their demand for input data.

The greatest challenge for multimedia fate models is to provide useful information without creating overwhelming demands for input data and producing outputs that can not be evaluated (OECD, 2004). When determining the purpose of the modeling study, the preferred precision of the models outcomes needs to be chosen, and to achieve that precision, the preferred spatial detail in model outcomes has to be defined. Which model detail is required, is partly dependent on the (expected) spatial variation in environmental concentrations in reality. Within this framework, the main goal of this thesis is to analyze the relative importance of the spatial variability in environmental conditions on the spatial variation in environmental concentrations. To this end, the aim is to indicate which factors influence the spatial variation in environmental concentrations, and to which extent they are of importance. Based on the insights obtained from this information, it will be easier to decide which spatial model resolution is desirable for a certain study, given the purpose of the study.

Chapters 2 and 3 describe and validate a method for incorporating depth-dependent soil concentrations in multimedia box models. In standard multimedia mass balance models, the soil compartment is modeled as a box with uniform concentrations, which does not correspond with actual field situations. Therefore, the theoretically expected decrease of soil concentrations with depth was implemented in the multimedia model SimpleBox 3.0. The effects of this implementation on the model outcomes were explored for nine compounds in four environmental compartments. For compounds with a low soil penetration depth (d_p), the new model predicts substantially higher or lower concentrations in the vegetation compartment than the old model. For those compounds, predicted concentrations in surface water and air were higher in the new model, but the deviations from the old model were smaller than in the vegetation compartment. For compounds with a large penetration depth, the model adaptations show little effect.

In Chapter 3, the predicted exponential soil concentration profiles are compared with measured soil concen-

trations to validate the method described in Chapter 2. In this paper, we explored the correspondence between the theoretically predicted soil concentration profiles and 84 field measured profiles. The theoretical concentration profiles could not be calculated directly, because for none of the measurement sites emission data were available. In order to enable a quantitative comparison between the calculated and the measured profiles, though, fits were made through the data points using an exponential vertical least square fitting procedure with the restriction of a fixed soil penetration depth (d_p). From this study it appeared that, in general, chemical concentrations in soils decline exponentially with depth. In half of the cases, values for the chemical specific soil penetration depth (d_p) were predicted within one order of magnitude. Over all, the reliability of multimedia models will improve when taking into account depth-dependent soil concentrations, the dp-values estimated either based on local conditions or on a fixed d_p-value, which we recommend to be 10 cm for chemicals with a log $K_{ow} > 3$.

Chapter 4 presents BasinBox, a newly developed steady-state generic multimedia fate model for evaluating risks of new and existing chemicals in river basins. The model concepts, as well as the inter-media processes quantified in the model, are outlined, and an overview of the required input parameters is given. To test the BasinBox model, calculations were carried out for predicting the fate of chemicals in the river Rhine basin. This was done for a set of 3175 hypothetical chemicals and three emission scenarios, i.e. to air, river water and cropland soils. For each of these hypothetical chemicals and emission scenarios, the concentration ratio between the downstream area and the upstream area was calculated for all compartments. From these calculations it appeared that BasinBox predicts significant concentration differences between upstream and downstream areas of the Rhine river basin for certain types of chemicals and emission scenarios. There is a clear trend of increasing chemical concentrations in downstream direction of the river basin. The calculations show that taking into account spatial variability between upstream, midstream and downstream areas of large river basins can be useful in the predictions of environmental concentrations by multimedia fate models.

Chapters 5 and 6 of this thesis describe two model inter-comparison studies between spatial and non-spatial environmental models. In the first study, a comparison is made between the non-spatial multimedia mass balance model SimpleBox and the spatially explicit model LOTOS-EUROS using PCB-153 as an example. The aim of this study was to determine whether nested generic box models can be used to predict spatial variance. We compared the two models concerning 1) average environmental concentrations, 2) spatial concentration variances, 3) spatial concentration patterns (maps), and 4) agreement with measured concentrations for the air and soil compartments. In SimpleBox, the spatial concentration variances and patterns were calculated subsequently for each separate grid cell surrounded by a regional and a continental shell with homogeneous, averaged circumstances. Average European PCB-153 concentrations calculated by LOTOS-EUROS and SimpleBox for the period 1981-2000 agree well for the air and soil compart-

ments. Moreover, the predicted concentrations of both models are in line with the measured PCB-153 concentrations in Europe during that period. For PCB-153, the prediction of spatial concentration variances with the nested multimedia fate model SimpleBox performs adequately in most cases, except for the lower concentration boundary in the air compartment. It is concluded that SimpleBox can be used to predict the spatial maximum and average concentrations of PCB-153 in the air and soil compartments. However, the proposed method has to be tested systematically for different types of compounds, emission scenarios, environmental compartments and spatial scales in order to allow conclusions about the general applicability of the method.

Chapter 6 of this thesis presents an inter-comparison study between the P_{ov} and LRTP estimates of seven different environmental models. Two different approaches to modeling the environmental fate of organic chemicals have been developed in the recent years. The first is the multimedia partitioning approach, which is generally applied in multimedia box or mass balance models. The second approach is based on the atmospheric dynamics and is applied in atmospheric transport models. Ideally, both types of models would yield the same outcomes for descriptors of overall persistence (P_{ov}) and long-range transport potential (LRTP). The main goal of the present study was to investigate if the multimedia mass balance models ClimoChem, SimpleBox, EVn-BETR, G-CIEMS, OECD-tool and the atmospheric transport models MSCE-POP and ADEPT predict the same rankings of the P_{ov} and LRTP of POPs, and to explain differences and similarities between the rankings by the mass distributions and inter-compartment mass flows. The study was performed for a group of 14 reference chemicals. With respect to P_{ov}, the models yield consistent results, which means that phase partitioning and degradation rates are described similarly by all model types. Concerning LRTP, there are larger differences between the models than for P_{ov}, due to different LRTP-calculation methods and spatial model resolutions. Between atmospheric transport models and multimedia fate models, no large differences in mass distributions and inter-compartment flows can be recognized. Deviations in mass flows are mainly caused by the geometrical design of the models.

In Chapter 7, the relative influence of substance properties and of environmental characteristics on the variation in concentrations of chemicals in Europe is compared for nine emission/receiving compartment scenarios. The classical box approach in multimedia mass balance models assumes that chemical properties largely determine the fate of substances in the environment. In this study, the relative influence of substance properties and of environmental characteristics on the variation in concentrations of chemicals in Europe was compared for nine emission/receiving compartment scenarios. This was done for a combination of 200 randomly selected organic chemicals and 137 realistic European regions, representing a 250x250 km spatial scale. Depending on the scenario, the range in predicted environmental concentrations spreads from 2 up to 9 orders of magnitude. Stepwise multiple regression analysis was performed to determine the contribution of each of the individual input parameters on the

total concentration variation. The assumption that the variation in the fate of chemicals in the environment mainly depends on substance specific partition coefficients and degradation rates, appeared to be valid. For the estimation of soil and water concentrations with direct emissions to these compartments, however, the influence of spatial variation in environmental characteristics should not be neglected in multimedia mass balance models.

All factors determining the spatial variation in environmental concentrations are summarized: the emissions (variation in emissions in space and in time, emission compartment), the physical-chemical substance properties, and the environmental conditions (variation in environmental conditions in space and in time, receiving compartment). The majority of these factors was subject of one or more of the studies presented in this thesis. Since not all factors indicated above were studied quantitatively, and since many relationships exist between the different factors, it is difficult to state which factor is the most important in determining the spatial variation in environmental concentrations. However, from the modeling studies presented in this thesis, it is possible to indicate qualitatively which factors are relatively important in most cases and which are not.
The spatial variation in emission intensities has been identified as the most influential parameter on the spatial variation in concentrations. The range in emissions is directly proportional to the concentrations and can mount up to several orders of magnitude, so it can easily overrule all other spatial factors. However, one should take into account that in case of diffuse, homogenously distributed emissions, this factor sometimes can be neglected. Also the physical-chemical properties, particularly K_h, K_{ow} and the degradation rate constants, of the substance under consideration play an important role, not only for its general environmental fate, but also for the spatial variation that occurs in environmental concentrations. The spatial variation in environmental conditions can also play a significant role, depending on the actual environmental conditions variability, and particularly in scenarios with emissions to water or soil, and if the water or soil compartment is considered. This factor becomes relatively important if emissions are distributed more homogeneously over the study area.

11 Samenvatting

Chemische stoffen kunnen schadelijk zijn voor de gezondheid van mensen en/of voor het functioneren van ecosystemen. Ontelbaar veel chemische stoffen zijn op de markt, ieder met zijn eigen emissiepatroon en fysisch-chemische eigenschappen. Door deze verschillen gedragen stoffen zich niet op dezelfde manier nadat ze zijn uitgestoten naar het milieu. Om het gedrag van stoffen in het milieu vast te stellen of te kunnen voorspellen, wordt vaak gebruik gemaakt van multimedia massabalansmodellen. In deze modellen wordt de omgeving weergegeven als een set van homogene 'dozen' of 'boxen', die elk een specifiek deel of compartiment van het milieu representeren (zoals lucht, water, bodem of biota). De concentratie van een stof in een zeker compartiment kan berekend worden door het oplossen van een set van massabalansvergelijkingen, die de modelprocessen van emissie, afbraak en stoftransport tussen de compartimenten beschrijven. Door de snelle opkomst van geografische informatiesystemen (GIS) worden sinds de jaren '90 ook ruimtelijk gedifferentieerde modellen ontwikkeld. Tegenwoordig wordt in veel multimedia massabalansmodellen rekening gehouden met de ruimtelijke variatie in milieukarakteristieken, maar tegelijkertijd worden de modellen hierdoor complexer en hebben zij een grotere hoeveelheid invoergegevens nodig.

Een grote uitdaging voor de makers van multimedia modellen is om bruikbare informatie te verschaffen zonder enorme hoeveelheden invoergegevens nodig te hebben en zonder resultaten te produceren die nauwelijks geëvalueerd kunnen worden. Bij het bepalen van het doel van een modelstudie, moet de gewenste precisie van de modeluitkomsten gekozen worden, en om die precisie te verkrijgen moet het gewenste ruimtelijke detail in de modellen worden bepaald. Wat het gewenste modeldetail is, is deels afhankelijk van de (verwachte) ruimtelijke variatie in stofconcentraties in de werkelijkheid. Dit proefschrift geeft antwoord op de vraag welke factoren van invloed zijn op de ruimtelijke variatie in milieuconcentraties van stoffen, en in welke mate elk van die factoren een rol speelt. Met deze informatie zal het eenvoudiger zijn te beslissen welke ruimtelijke modelresolutie wenselijk is, afhankelijk van het doel van die studie.

Hoofdstukken 2 en 3 beschrijven en valideren een methode om diepte-afhankelijke bodemconcentraties op te nemen in multimedia modellen. In standaard multimedia massabalansmodellen wordt de bodem voorgesteld als een box met uniforme concentraties, terwijl concentraties in de bodem sterk kunnen afnemen met de diepte. Daarom is een exponentiële afname van bodemconcentraties met de diepte geïmplementeerd in het multimedia model SimpleBox 3.0. De effecten van deze modelaanpassing op de modeluitkomsten zijn geanalyseerd voor negen stoffen in vier compartimenten. Voor stoffen met een kleine bodempenetratiediepte (d_p) voorspelt het nieuwe model substantieel hogere of lagere concentraties in het vegetatiecompartiment dan in het oude model. Voor diezelfde stoffen zijn de voorspelde concentraties in water en lucht hoger in het nieuwe model, maar de verschillen met het oude model zijn in deze compartimenten minder prominent. Voor stoffen met een grote penetratiediepte vertonen de modelaanpassingen weinig effecten op de modelvoorspellingen.

In hoofdstuk 3 worden de voorspelde exponentiële bodemconcentratieprofielen vergeleken met meetgegevens. Voor dit doel zijn 84 in het veld gemeten bodemconcentratieprofielen verzameld uit de literatuur. Uit deze studie blijkt, dat stofconcentraties in de bodem over het algemeen afnemen met de diepte volgens een exponentieel patroon. In de helft van de gevallen komt de voorspelde en de gemeten penetratiediepte overeen binnen een orde van grootte. In het algemeen kan gesteld worden, dat de betrouwbaarheid van multimedia modellen zal verbeteren als diepte-afhankelijke bodemconcentraties worden meegenomen in de voorspellingen. De waarde voor de bodempenetratiediepte kan het best bepaald worden aan de hand van lokale omstandigheden. Als die niet beschikbaar zijn, wordt voor stoffen met een log K_{ow}>3 een vaste penetratiediepte van 10 cm geadviseerd.

Hoofdstuk 4 presenteert BasinBox, een nieuw 'steady-state' generiek multimedia model om het gedrag van stoffen in rivierstroomgebieden te berekenen. In het BasinBox model wordt een rivierstroomgebied onderverdeeld in een boven-, midden- en benedenstroomsgebied, ieder met binnendijkse en buitendijkse delen. Om het BasinBox-model te testen, zijn berekeningen uitgevoerd met het model voor het Rijnstroomgebied. Dit is gedaan voor een set van 3175 hypothetische stoffen en drie emissiescenario's naar lucht, rivierwater en landbouwbodems. Uit deze berekeningen blijkt, dat BasinBox voor een aantal stoffen significante concentratieverschillen voorspelt tussen het boven- en benedenstrooms gebied. Er is een duidelijke trend zichtbaar van stijgende stofconcentraties in benedenstroomse richting. De gemaakte berekeningen geven aan, dat het zinvol kan zijn de ruimtelijke variatie tussen boven-, midden- en benedenstroomse gebieden van grote stroomgebieden mee te nemen in concentratievoorspellingen met multimedia massabalans-modellen.

Hoofdstukken 5 en 6 van dit proefschrift beschrijven twee vergelijkingsstudies tussen ruimtelijke en niet-ruimtelijke modellen. In de eerste studie is een vergelijking gemaakt tussen het niet-ruimtelijke multimedia massabalansmodel SimpleBox en het ruimtelijk expliciete model LOTOS-EUROS met PCB-153 als voorbeeldstof. Het doel van de studie was om vast te stellen of geneste, generieke box modellen kunnen worden gebruikt om ruimtelijke variantie in stofconcentraties te voorspellen. Hiertoe zijn de twee modellen vergeleken voor wat betreft hun 1) gemiddelde milieuconcentraties, 2) ruimtelijke concentratievarianties, 3) ruimtelijke concentratiepatronen (kaarten), en 4) de overeenkomst met gemeten concentraties. In SimpleBox zijn de ruimtelijke concentratievariaties achtereenvolgens berekend voor elke individuele lokale cel, die wordt omringd door een regionale en een continentale schil met homogene, gemiddelde omstandigheden. Gemiddelde Europese PCB-153 concentraties voor de periode 1981-2000 zijn overeenkomstig voorspeld door SimpleBox en LOTOS-EUROS in de lucht- en bodemcompartimenten. Bovendien zijn de voorspelde concentraties in lijn met de gemeten PCB-153 concentraties gedurende die periode. De methode om ruimtelijke concentratievariaties te voorspellen met het SimpleBox model voldoet dus in de meeste gevallen voor PCB-153, behalve voor de cellen met lage luchtconcentraties, en het is dus mogelijk om met SimpleBox ruimtelijke maximum en gemiddelde con-

centraties te bepalen in lucht en bodem. Voordat de algemene toepasbaarheid van de rekenmethode vastgesteld kan worden, zullen eerst meer berekeningen uitgevoerd moeten worden voor verschillende typen stoffen, emissiescenario's, milieucompartimenten en ruimtelijke schalen.

In hoofdstuk 6 wordt een vergelijkingsstudie gepresenteerd tussen zeven verschillende milieumodellen: de multimedia massabalansmodellen ClimoChem, SimpleBox, EVn-BETR, G-CIEMS en OECD-tool en de atmosferische transport modellen MSCE-POP and ADEPT. De modellen zijn vergeleken ten aanzien van de voorspelde rangorde voor de overall persistentie (P_{ov}) en lange-afstand transport potentiaal (LRTP) van 14 POP-stoffen. Ten aanzien van de P_{ov}, vertonen de modellen overeenkomstige resultaten, wat betekent dat de verdelingen van stoffen over fasen en de afbraaksnelheden van stoffen in verschillende fasen min of meer gelijk worden beschreven door alle modellen. Ten aanzien van LRTP zijn grotere verschillen tussen de modellen zichtbaar dan voor P_{ov}. De belangrijkste redenen hiervoor zijn het verschil in de LRTP-berekeningswijze die de verschillende modellen hanteren en de verschillende ruimtelijke resoluties van de modellen. In het algemeen kunnen geen grote verschillen geconstateerd worden tussen de modelvoorspellingen van atmosferische transportmodellen en multimedia massabalansmodellen. Verschillen in voorspelde massaverdelingen worden voornamelijk veroorzaakt door de geometrische inrichting van de modellen.

In hoofdstuk 7 wordt de relatieve invloed van stofeigenschappen en van milieukarakteristieken op de variatie in concentraties van stoffen vergeleken. De klassieke 'box' model benadering in multimedia massabalansmodellen veronderstelt dat stofeigenschappen voor een groot deel het gedrag van stoffen in het milieu bepalen. De mogelijke invloed van milieukenmerken wordt in deze modellen nauwelijks meegenomen doordat gemiddelde milieucondities worden gemodelleerd. Of dit terecht is, is in hoofdstuk 7 onderzocht door de relatieve invloed van stofeigenschappen en van milieukarakteristieken op de variatie in concentraties van stoffen in Europa vast te stellen. Dit is gedaan voor negen scenario's met combinaties van emissiecompartiment (lucht, water, bodem) en ontvangend compartiment (lucht, water, bodem), voor 200 willekeurig gekozen organische stoffen en 137 Europese regio's op een 250x250 km schaal.
Afhankelijk van het modelscenario is de spreiding in voorspelde milieuconcentraties twee tot negen ordes van grootte. Stapsgewijze multiple regressie analyse is uitgevoerd om de bijdrage van elk van de individuele invoerparameters op de totale concentratievariatie vast te stellen. Het blijkt dat de variatie in milieuconcentraties van stoffen inderdaad voornamelijk afhankelijk is van stofeigenschappen. Voor het bepalen van bodem- en waterconcentraties met directe emissies naar deze compartimenten zou echter ook de invloed van de ruimtelijke variatie in milieukarakteristieken meegenomen moeten worden in multimedia massabalansmodellen.

Alle factoren die de ruimtelijke variatie in milieuconcentraties van stoffen beïnvloeden zijn samengevat in de discussie van dit proefschrift: 1) de emissies (variatie in emissies in de ruimte en in de tijd, emissiecompar-

timent), 2) de fysisch-chemische stofeigenschappen en 3) de milieucondities (variatie van milieucondities in de ruimte en in de tijd, doelcompartiment). Het merendeel van deze factoren is aan de orde gekomen in een of meer studies in dit proefschrift. Het is mogelijk om op basis van de studies uit dit proefschrift kwalitatief een indicatie te geven welke factoren relatief het meest van belang zijn en welke niet. De ruimtelijke variatie in emissie-intensiteiten wordt aangemerkt als de meest bepalende factor in de ruimtelijke variatie in concentraties. De spreiding in emissies in de ruimte staat direct in verhouding tot de spreiding in concentraties en kan oplopen tot meerdere ordes van grootte. Men moet er echter rekening mee houden, dat in het geval van diffuse, homogeen verspreide emissies, deze factor niet of nauwelijks invloed heeft. Ook de fysisch-chemische eigenschappen van de te onderzoeken stof, vooral K_h, K_{ow} en de afbraaksnelheden, spelen een belangrijke rol. Niet alleen bij de bepaling van het algemene lot van een stof in het milieu, maar ook voor de ruimtelijke variatie die optreedt in milieuconcentraties. Daarnaast kan de ruimtelijke variatie in milieucondities een significante rol spelen, afhankelijk van de mate waarin de milieukarakteristieken ruimtelijk verschillen. Deze factor speelt vooral een rol in scenario's waarin emissies plaatsvinden naar water of bodem en waarin water- of bodemconcentraties worden berekend.

12 List of publications

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Anne Hollander, Alberto Pistocchi, Mark A.J. Huijbregts, Ad M.J. Ragas, Dik van de Meent, 2008. Substance or space? The relative importance of substance properties and environmental characteristics in modeling the fate of chemicals in Europe.
Submitted to *Envionmental Toxicology and Chemistry*.

Anne Hollander, Martin Scheringer, Victor Shatalov, Elena Mantseva, Andy Sweetman, Michiel Roemer, Noriyuki Suzuki, Fabio Wegmann, Dik van de Meent, 2008. Estimating overall persistence and long-range transport potential of persistent organic pollutants: seven multimedia mass balance models and atmospheric transport models in comparison.
Submitted to *Journal of Environmental Monitoring*.

13 Bedankt!

13 juni 2008. Het manuscript is al een tijdje goedgekeurd, en rondom mijn proefschrift hoeven alleen nog maar de puntjes op de i gezet te worden. Vader is druk met de lay-out, voor mij staat nog het schrijven van een dankwoord op het lijstje. Mooi moment om terug te blikken op vijf jaar aioschap in Nijmegen en de mensen die daarbij horen.

Wat heb ik vaak zitten mopperen op zondagavond als de nieuwe werkweek weer voor de deur stond. Ik baalde van het vooruitzicht van vroeg op, lang reizen, hele dagen binnen zitten, moeilijk werk te doen, terwijl ik nog zoveel andere leukere en op dat moment belangrijkere klusjes kon bedenken. Gelukkig kwam ik in de loop van de maandag altijd weer een beetje in het ritme en was de rest van de week in Nijmegen lang niet zo'n ramp als leek op zondagavond. En nu, nu ik terugkijk op de hele periode, overheerst toch het goede gevoel: ik heb heel veel geleerd, onderwijservaring opgedaan, samengewerkt met leuke mensen, interessante congressen bezocht en mooie reisjes gemaakt. Ik ben blij dat ik als aio bij milieukunde heb kunnen werken!

Ad, Dik en Mark waren mijn drie belangrijkste begeleiders. Met mij erbij een aardig kwartet van eigenzinnige, of zeg maar eigenwijze mensen. Toch ging dat bijna altijd zonder problemen. Dik, jij was de beste promotor die ik had kunnen wensen. Hoe vaak heb ik niet verhalen van andere aio's aangehoord, die klaagden over hun promotor, omdat hij schitterde in afwezigheid, alleen maar uit was op eigen succes of zijn aio's afblafte. Ik kon die verhalen nooit beamen… Behalve dat je me veel kennis en inzicht hebt bijgebracht in het multimedia modelleren, heb ik zelden iemand gekend die zo eerlijk, oprecht en begaan was als jij, zowel in het werk als (ver) daarbuiten. Ik hoop dat ik daar ook nog wat van opgestoken heb de afgelopen tijd. Ik vond het een eer je allereerste aio te mogen zijn en ben blij dat ik ook na mijn promotie nog met je samen mag blijven werken!

Mark en Ad, ook door jullie heb ik heel veel geleerd van het modelleervak en van de milieukunde in het algemeen. Mark, jouw fanatisme was fantastisch. Ongelooflijk hoeveel werk jij kunt verzetten en met hoeveel spirit jij altijd maar aan de gang kunt blijven. Die gedrevenheid heeft mij vaak gemotiveerd om ook nog even door te gaan, iets af te maken of iets op te pakken. Ad, aan jou waardeerde ik vooral jouw vermogen om mijn werk, als ik het allemaal wel welletjes vond, nog eens met een blanco blik te bekijken en kritisch te zijn op gehanteerde methoden of formuleringen van zinnen. Als ik jouw commentaar verwerkt had, werd een artikel altijd mooier en beter. Heel veel dank aan jullie beide voor de tijd en moeite die jullie als co-promotoren in mij en dit proefschrift gestoken hebben!

Buiten deze drie begeleiders was er natuurlijk de hele afdeling Milieukunde van de Radboud Universiteit, eerst onder Piet Nienhuis, gevolgd door Rob Leuven en Jan Hendriks. Op de kamer met Sander, later Jasper en Karin B. en uiteindelijk, als 'ouwe aio's' veel schik gehad met Karin V. en Arie. Bedankt ook de studenten die stage gelopen hebben: Laurens Hessels, Josef Dufek, Irmgard Henning, Frederiek Sperna-Weiland en Iris Baijens. Het werk dat jullie deden was steeds weer een klein bouwsteentje voor een hoofdstuk uit dit proefschrift; Laurens en Iris, samen met jullie zijn daar mooie artikelen uitgekomen. Harrie Hendriks bedankt voor je advies over statistische procedures, Pim de Voogt als co-auteur van het eerste artikel en Ferd Sauter voor je knappe LOTOS-EUROS modelleerwerk.

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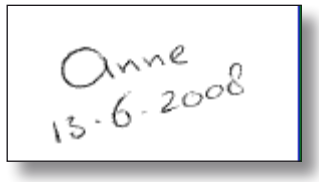
Ik had het geluk dat ik al een jaar voor het afronden van het proefschrift bij het Laboratorium voor Ecologische Risicobeoordeling (LER) van het RIVM kon komen werken. Buiten het feit dat dit veel dichter bij huis is dan Nijmegen en dus goed te befietsen, heb ik LER en het RIVM dat eerste jaar als een heel prettige werkplek ervaren. Fijne collega's van LER, en ook mensen van LVM en SEC, bedankt! Hopelijk is er na mijn promotie meer tijd om mooie projecten met jullie samen te gaan draaien.

Naast het werk waren er alle lieve en leuke mensen van de korfbal, en van HKC 1 en 2 in het bijzonder, van de bijenvereniging, vrienden en studiegenootjes, tennis- en zwemmaatjes, papa en mama, oma's en opa's en andere familieleden. Myrthe en Ananda, ook al zijn er wel eens perioden dat we elkaar weinig zien, fijn dat we nog steeds goede vriendinnen zijn, en bedankt dat jullie als paranimf wilden optreden. Papa bedankt voor al het werk dat je in de vormgeving van dit boekje gestoken hebt, het is prachtig geworden, en mama voor al het werk in de tuin en de bijen. Iedereen om mij heen bedankt voor de fijne tijd en op naar volgende uitdagingen!



14 Curriculum vitae

Anne Hollander werd geboren op 3 juni 1979 in Utrecht. Na acht jaar op basisschool De Hoge Raven en zes jaar op OBS Hendrik van der Vlist, later Prisma College, in Utrecht deed zij in 1997 eindexamen gymnasium. In september van dat jaar ging zij fysische geografie studeren aan de Universiteit Utrecht. Zij specialiseerde zich in de doctoraalfase in de richting bodem- en waterbeheer. Haar afstudeeronderzoek werd uitgevoerd in samenwerking met Vereniging Natuurmonumenten en richtte zich op het inventariseren van mogelijke hydrologische herstelmaatregelen in het Wooldse Veen bij Winterswijk. Een gecombineerde veldwerk- en modelstudie. De studie fysische geografie werd afgesloten met een stage aan de Tomsk University in Siberië, Rusland. Daar werd met behulp van remote sensing en veldgegevens het Vasyugan hoogveensysteem in kaart gebracht. In 2002 studeerde zij af (cum laude).

In januari 2003 startte Anne een promotieonderzoek aan de vakgroep Milieukunde van de Katholieke Universiteit Nijmegen, op het gebied van multimedia fate modellen, waar dit proefschrift het belangrijkste resultaat van is. In in die periode heeft zij ook meegewerkt aan de ontwikkeling van de onderwijsmodule 'schakelblok milieuchemie: gedrag van stoffen' en heeft zij diverse andere college's, praktica en een studentenexcursie naar Polen verzorgd.

Sinds april 2007 werkt ze in deeltijd bij het Rijksinstituut voor Volksgezondheid en Milieu (RIVM) bij het Laboratorium voor Ecologische Risicobeoordeling en nog in deeltijd aan de Radboud Universiteit Nijmegen.

Naast deze werkzaamheden heeft Anne een eigen bedrijfje 'Fiks', waarin zij voornamelijk actief is in de thuiszorg en het verbouwen, verwerken en verkopen van biologische streekproducten (www.tuin-brassica.nl). Zij is gediplomeerd imker en heeft het diploma voor de basisopleiding verzorgende individuele gezondheidszorg.